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MODENA

Deliverable 3.2

Simulations for foams, dispersion and mixing and
developed SW

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Description of deliverable

The main objective of the deliverable is to describe the developed software for solving rheology, coalescence and nucleation models. The `TFEM` software developed at the TU/e forms the basis of the surrogate models which are integrated into the MoDeNa framework. At POLITO the `QMOMFoamKin` is the openFoam solver developed within MoDeNa for the macroscopic simulation of the flow of the polyurethane (PU) foam. The macroscopic simulation requires input in the form of surrogate models. If either the rheology or the coalescence surrogate models are called with parameters out of bound for these models, an option is provided to run the detailed model.

The Software described in this document is written with `TFEM`. `TFEM` is a toolkit for the finite element method (fem). It is written in Modern Fortran. The core of `TFEM` is moderately sized and it is intended to be used in education and research.

With these components into place, inputs from WP1 and WP2 (including physical properties, property methods, reaction kinetics and equations of state) can be processed as well. Furthermore, a description of concepts in macro-tools for initial dispersion of reactants, bubble initiation, solidification of cell walls and cell coalescence/wall drainage can be completed, as well as descriptions of suitable validation procedures. Moreover, tools for simulation of application mechanical and transport properties including their deterioration will be adopted or developed.

Summary of contribution of involved partners to deliverable

The main activities so far in this work package have been carried out by Partners POLITO, and TU/e. Other partners active in this work package are IMDEA and BASF, but their main activities are not directly related to solving rheology, coalescence and nucleation models. This will start during the next period when the connection to the mechanics of the foam at a macroscopic level starts to be important.

At IMDEA work has been carried out to determine the different strategies to model the 3D structure of the foam. The result of the analysis was to begin from statistical information about the cell size, shape, number of faces, (thus information coming from X-ray micro tomography or provided by models at lower length scales) and built a statistically-equivalent microstructure using the appropriate software. The models at the lower length scales actively couple with the developments in WP2 and even at the micro scale in WP1. At the TU/e we also started to analyze the possible formulations of constitutive equations to model the polymer in the foam at the continuum level.

At POLITO the activities in Work package 3 are concentrated on the development and implementation of an open source modeling technique for Polyurethane Foams (PU). In order to achieve the objective of MODENA project for WP3, the macro-scale CFD tool is founded on OpenFOAM CFD code. Amongst various solvers implemented in OpenFOAM, solvers in which the Volume of Fluid (VOF) approach is utilized have been selected for further investigations and modifications. As the complex multiphase system is considered to be constituted by two immiscible fluids, the VOF approach is able to capture the interface between the expanding PU foam and its surroundings.

At TU/e activities are started which are on the border of Workpackages 2 and 3. In particular we are modeling the foam which is treated as a compound drop, thus a drop contains multiple drops inside. The methods we are applying rely on explicit tracking of the interface and have main benefit that the very narrow liquid bridges accurately described. The software as developed at this stage is already rather general but will be adapted it the second have of the project to include more complex rheology of the polymer as well as interface transport that effects interfacial tension and leads to Marangoni effects.

QMOMFoamKin

QMOMFoamKin is the openFoam solver developed within MoDeNa for the macroscopic simulation of the flow of the polyurethane (PU) foam. Together with the corresponding solver under development in Fluent is one of the pieces of software produced by the research efforts in WorkPackage3. QMOMFoamKin (as its Fluent counterpart) is based on a volume-of-fluid (VOF) solver. In openFoam two are the main VOF solvers available: “interFoam” and “compressibleinterFoam”. Since the foam is a variable density flow the solver “compressibleinterFoam” has been selected as starting point for the development of QMOMFoamKin. Some tests have been also carried out with the solver “interFoam” and their results will be reported in future documents.

In QMOMFoamKin the foam is described as a pseudo-homogeneous fluid with varying properties (i.e. density, viscosity, conductivity, etc.). The evolution of the interface between the foam and the external gas (i.e. air) is tracked, as mentioned, by using the VOF method. The two coexisting phases, foam and gas, are described through their volume fractions, α_F and α_G , and densities, ρ_F and ρ_G . As well-known volume fractions sum to unity:

$$\alpha_F + \alpha_G = 1$$

and obey the continuity equation (written here for the foam only):

$$\frac{\partial}{\partial t}(\alpha_F \rho_F) + \nabla \cdot (\alpha_F \rho_F \mathbf{U}_F) = 0$$

This equation is solved together with a momentum balance equation:

$$\frac{\partial}{\partial t}(\rho \mathbf{U}) + \nabla \cdot (\rho \mathbf{U} \mathbf{U}) = -\nabla p + \rho \mathbf{g} + \nabla \cdot [\mu(\nabla \mathbf{U}) + (\nabla \mathbf{U})^T]$$

where:

$$\rho = \alpha_F \rho_F + \alpha_G \rho_G$$

and:

$$\mu = \alpha_F \mu_F + \alpha_G \mu_G$$

The interface between the foam and the surrounding gas is reconstructed using different techniques and the details of this reconstruction is omitted here for the sake of brevity (Greenshields et al., 1999)¹.

On the VOF solver a number of additional equations have been added. One of them is the transport equation for the conversion of the gelling reaction, X_{OH} :

¹ Greenshields, C.J., Weller, H.G., Ivankovic, A. The finite volume method for coupled fluid flow and stress analysis (1999) Computer Modeling and Simulation in Engineering, 4 (3), pp. 213-218.

$$\frac{\partial}{\partial t}(\rho X_{OH}) + \nabla \cdot (\rho \mathbf{U} X_{OH}) = \rho \left[A_{OH} \exp\left(\frac{E_{OH}}{RT}\right) c_{OH}^0 (1 - X_{OH}) \left(\frac{c_{NCO}^0}{c_{OH}^0} - 2 \frac{c_W^0}{c_{OH}^0} X_W - X_{OH} \right) \right]$$

where A_{OH} and E_{OH} are the pre-exponential factor and the activation energy, R is the gas constant, T is the absolute temperature and c_{NCO}^0 , c_{OH}^0 and c_W^0 are the initial molar concentrations of isocyanate, polyol and water in the reacting foam. This equation is implemented together with the transport equation for the conversion of the blowing reaction, X_W :

$$\frac{\partial}{\partial t}(\rho X_W) + \nabla \cdot (\rho \mathbf{U} X_W) = \rho \left[A_W \exp\left(\frac{E_W}{RT}\right) (1 - X_W) \right]$$

where A_W and E_W are the pre-exponential factor and the activation.

The blowing reaction produces carbon dioxide (and urea) that diffuses from the bulk of the liquid to the gas bubbles. The mass fraction of carbon dioxide in the liquid of the foam can therefore be calculated as follows:

$$\frac{\partial}{\partial t}(\rho w_{CO_2}) + \nabla \cdot (\rho \mathbf{U} w_{CO_2}) = \rho \left[c_W^0 \frac{dX_W}{dt} \frac{M_{CO_2}}{\rho_P} - \bar{G}_1^{CO_2} \frac{P}{RT} \frac{M_{CO_2}}{\rho_P} \right]$$

where P is the system pressure, ρ_P is the density of the polymerizing liquid mixture (generally assumed constant and equal in this work to 1100 kg/m³) and $\bar{G}_1^{CO_2}$ is the moment of order one of the growth rate due to carbon dioxide diffusion and will be explained in details later on.

The mixture undergoing polymerization also contains the physical blowing agent that evaporates due to the temperature raise. The mass fraction of the physical blowing agent in the liquid of the foam can be calculated by solving the following equation:

$$\frac{\partial}{\partial t}(\rho w_{BL}) + \nabla \cdot (\rho \mathbf{U} w_{BL}) = \rho \left[-\bar{G}_1^{BL} \frac{P}{RT} \frac{M_B}{\rho_P} \right]$$

where \bar{G}_1^{BL} is the moment of order one of the growth rate due to the diffusion of the blowing agent and will also detailed later on. The temperature of the system is calculated by solving the enthalpy balance as implemented in “compressibleinterfoam” by introducing in the source term the heat of the blowing and gelling reactions (related to ΔH_W and ΔH_{OH}) and the latent heat of evaporation of the blowing agent (related to λ).

QMOMFoamKin also implements a population balance equation (PBE), which describes the evolution of the bubble size distribution (BSD) of the bubbles, or cells, of the foam. This function is defined in such a way that: $n(v, t)dv$, represents the number of bubbles with volume in the infinitesimal size range between v and $v + dv$, per unit volume of the liquid mixture undergoing polymerization. Very often instead of tracking the evolution of the BSD the problem is reformulated in terms of the moments of the BSD. The generic moment of order k is defined as follows:

$$m_k(t) = \int_0^{+\infty} n(v, t) v^k dv$$

Being the polyurethane foam constituted by the liquid and the gas bubbles, in order to estimate the moments of the BSD per unit volume of the foam the following transform is necessary:

$$M_k(t) = \frac{m_k(t)}{1 + m_1(t)}$$

where M_k is the moment of the BSD based on the total volume of the foam. By using this notation the density of the foam can be readily calculated as follows:

$$\rho_F(t) = \rho_G \left[\frac{m_1(t)}{1 + m_1(t)} \right] + \rho_P \left[\frac{1}{1 + m_1(t)} \right]$$

where ρ_G is the density of the gas constituting the bubbles (generally calculated with the ideal gas law) whereas ρ_P is the density of the liquid mixture.

The evolution of the BSD is dictated by the PBE that reads as follows (time dependencies are omitted for brevity):

$$\begin{aligned} \frac{\partial}{\partial t} (\rho n(v)) + \nabla \cdot (\rho \mathbf{U} n(v)) + \frac{\partial}{\partial v} [\rho G(v) n(v)] \\ = \rho \left[\frac{1}{2} \int_0^v \beta(v, v-v') n(v) n(v-v') dv' - \int_0^{+\infty} \beta(v, v') n(v) n(v') dv \right] \end{aligned}$$

where G is the so-called bubble growth rate and β is the bubble coalescence kernel.

The bubble growth rate is due to the diffusion of the physical blowing agent and of the carbon dioxide molecules to the gas bubbles of the foam. Although several detailed models can be formulated, in this work a very simple approach will be used. The overall growth rate is calculated as the summation of the growth rate due to the blowing agent:

$$G^{BL}(v) = c_{BL} \left(\frac{w_{BL} - w_{BL}^D}{w_{BL}^D} \right)$$

and due to carbon dioxide:

$$G^{CO_2}(v) = c_{CO_2} \left(\frac{w_{CO_2} - w_{CO_2}^D}{w_{CO_2}^D} \right)$$

where w_{BL} and w_{CO_2} are the mass fractions of blowing agent and carbon dioxide in the liquid phase of the foam, c_{BL} and c_{CO_2} are model constants varied in this work between 10^{-14} and 10^{-12} m³/s, whereas w_{BA}^D and $w_{CO_2}^D$ are the corresponding equilibrium concentrations (which depend on the system temperature, T).

Bubble coalescence is caused by the relative motion of the bubbles, due to shear and velocity gradients, that inevitably are imposed during the expansion of the foam, resulting in the following kernel:

$$\beta(v, v') = \beta_0(v + v')$$

where β_0 depends on the flow. The PBE is solved here with the Quadrature Method of Moments (QMOM) and details are omitted for the sake of brevity (Marchisio et al. 2003)².

² Marchisio, D.L., Vigil, R.D., Fox, R.O. Quadrature method of moments for aggregation-breakage processes (2003) *Journal of Colloid and Interface Science*, 258 (2), pp. 322-334.

Mathematical Model Description for Tool for Rheology and Coalescence

For both the Coalescence Kernel and the Rheology Tools a similar underlying model is used which relies on a Stokes flow approach for incompressible fluids where we explicitly describe both components in full detail during flow. This option gives us the direct possibility to couple micro structure evolution with rheology. For both phases, i.e. the bubbles and the outer fluid it is assumed at this stage that inertia can be neglected and that the volume is constant (which is appropriate within the MoDeNa project). Note that this adaptation is only minor and without any restriction we can add stationary and instationary inertia.

As a result the mass and the momentum balance for both phases reduce to

$$\nabla \cdot \mathbf{u} = 0 \quad (1)$$

$$\nabla \cdot \boldsymbol{\sigma} = 0 \quad (2)$$

the \mathbf{u} and $\boldsymbol{\sigma}$ are the velocity vector and the full Cauchy stress tensor defined in the full domain. For fluids the stress tensor $\boldsymbol{\sigma}$ can be written as:

$$\boldsymbol{\sigma} = -p\mathbf{I} + \mathbf{T} \quad (3)$$

where p is the pressure, \mathbf{I} is the identity tensor and \mathbf{T} is the extra stress tensor. The model is capable of simulating fluids with different types of rheology, i.e. non-Newtonian rheology and thus also viscoelastic fluid behaviour. Thus within either phase we have completely independent rheology, i.e. Newtonian, inelastic non-Newtonian or full viscoelastic non-Newtonian.

The rheological behaviour of the polymer will come from input WP2 and without complexity can be included in our Software. For now only the case of Newtonian fluid is studied.

Therefore, \mathbf{T} can be expressed as:

$$\mathbf{T} = 2\eta_i\mathbf{D} \quad (4)$$

with η_i the viscosity in either one of the two phases and \mathbf{D} the symmetric part of the velocity gradient tensor.

The gas inside the bubbles is assumed to be an incompressible gas. For that reason we impose constant volume constraint on n-1 bubble interfaces

$$\int_{A_b} \mathbf{u} \cdot \mathbf{n} = 0$$

Thus inside one bubble we have zero pressure and for the rest the pressure compensates so that the volume remains constant.

Rheology tool

The Rheology tool aims on calculating the rheological properties of the liquid foam. By using the same model one can study the behaviour of 5-10 bubbles in a box under shear flow. Figure 1 shows the deformation of a collection of sliding bi-periodic boxes under shear flow that are initially distributed regularly. With this approach a small number of bubbles could represent the whole system that contains a huge number of bubbles. In Figure 2 we can see the initial configuration of a representative frame containing 8 bubbles. After the field computation, the integration of stresses is performed over the fluid domain in order to calculate the bulk stress according to the Batchelor formula.

$$\langle \boldsymbol{\sigma} \rangle = \frac{1}{A} \int_{A_f} \boldsymbol{\sigma} dA - \frac{\Gamma}{A} \int_A (\mathbf{n}\mathbf{n} - \mathbf{I}) dA \quad (5)$$

By having the average stress one can calculate the rheological properties of the fluid such as the viscosity.

For detailed information about the numerical methods and techniques that have been used for the implementation of the tools we refer to Milestone 3.1 report that contains an extended description.

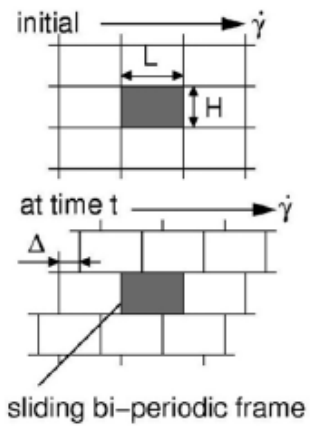


Figure 1: Sliding bi-periodic frame as a representative computational domain in shear flow.

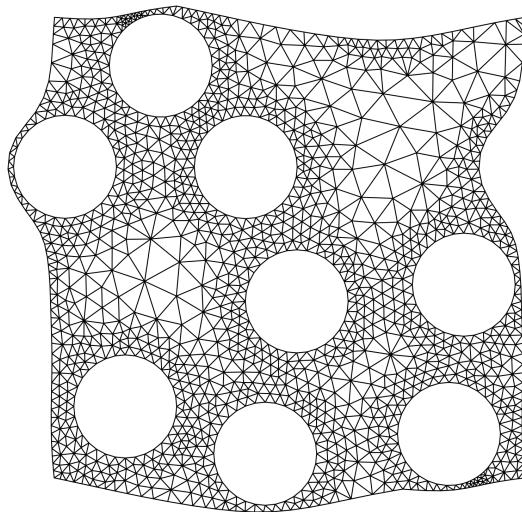


Figure 2: Initial configuration of a representative bi-periodic frame containing 8 bubbles.

Surrogate model

The surrogate model uses the Carreau-Yasuda model to fit the data obtained from the detailed model

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty})[1 + (\lambda\dot{\gamma})^{\alpha}]^{\frac{n-1}{\alpha}}$$

where λ the relaxation time, parameters α , n and η_{∞} and η_0 the viscosity at infinite and zero shear rate, respectively. For now the model is used to fit data from BASF.

Table 1: Carreau-Yasuda model fitting parameters.

Temperature	η_0	η_{∞}	λ	n	α
25°C	212.948	0	10	1.0328	2
50°C	82.6644	2171.44	4.3163	1.0027	1.6337

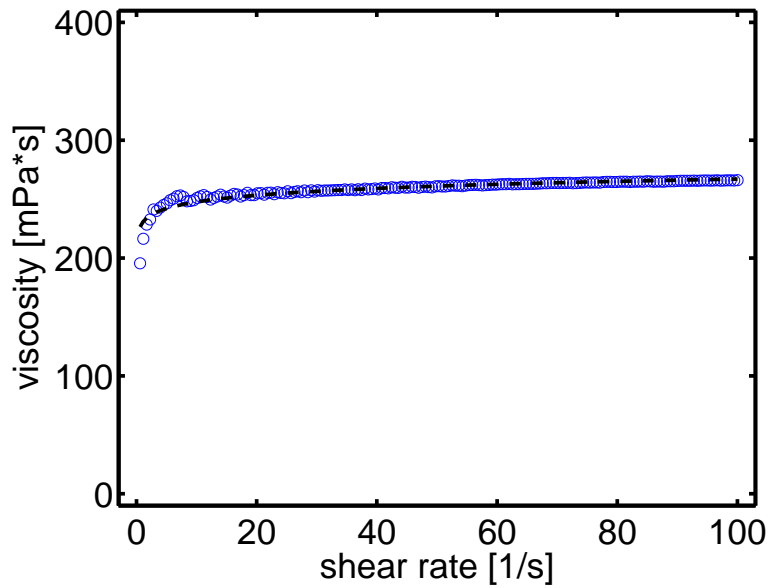


Figure 3: Viscosity as a function of shear rate at 25°C.

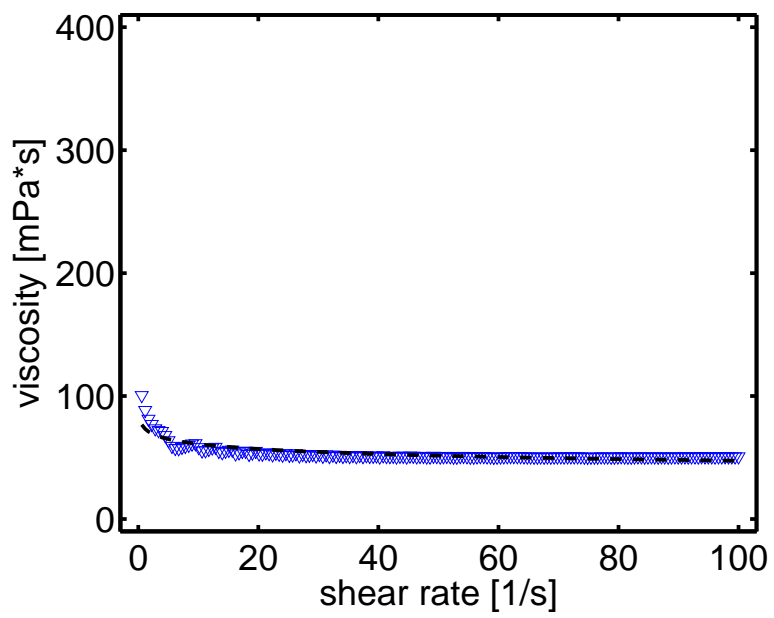


Figure 4: Viscosity as a function of shear rate at 50°C.

Results

While there are still some instabilities we were able to extract some first results from the Rheology tool and compare them with analytical results from the literature. In Figure 5 and 6 we plot the xy component of the stress tensor and the normal stress difference of a mono-disperse suspension of bubbles with volume fraction $\phi = 0.14$ and Capillary number $Ca=0.16$. The suspension is sheared under constant shear rate $\dot{\gamma} = 1$.

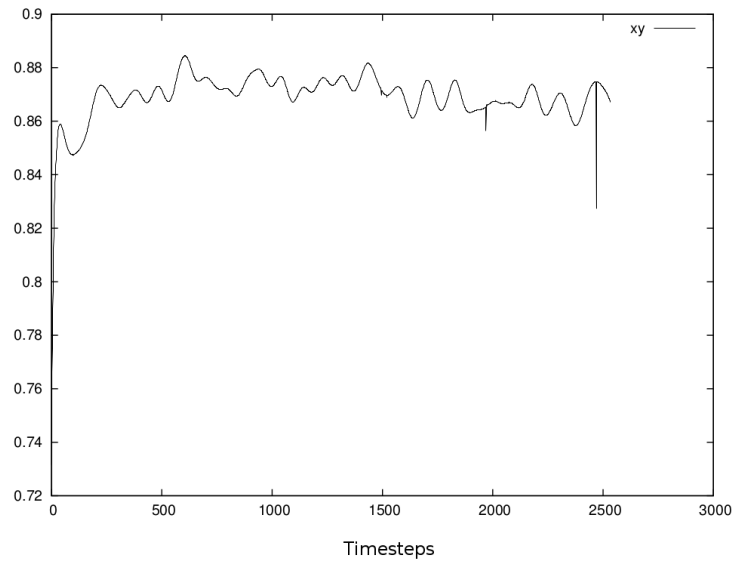


Figure 5: xy component of the stress tensor over time of a mono-disperse suspension of bubbles with volume fraction $\phi = 0.14$ and Capillary number $Ca=0.16$.

For steady flow, the relative viscosity is given by Mader et al. [1]

$$\eta_{r,b} \equiv \frac{\eta_b}{\mu} = \eta_{r,\infty} + \frac{\eta_{r,0} - \eta_{r,\infty}}{1 + ((6/5)Ca)^2}$$

where η_b is the apparent viscosity of the bubble suspension, and $\eta_{r,0}$ and $\eta_{r,\infty}$ are the relative viscosity of the bubble suspension at low and high Ca , respectively. For non-dilute suspensions $\eta_{r,0}$ and $\eta_{r,\infty}$ are given by Mader et al. [1]

$$\eta_{r,0} = (1 - \phi_b)^{-1}$$

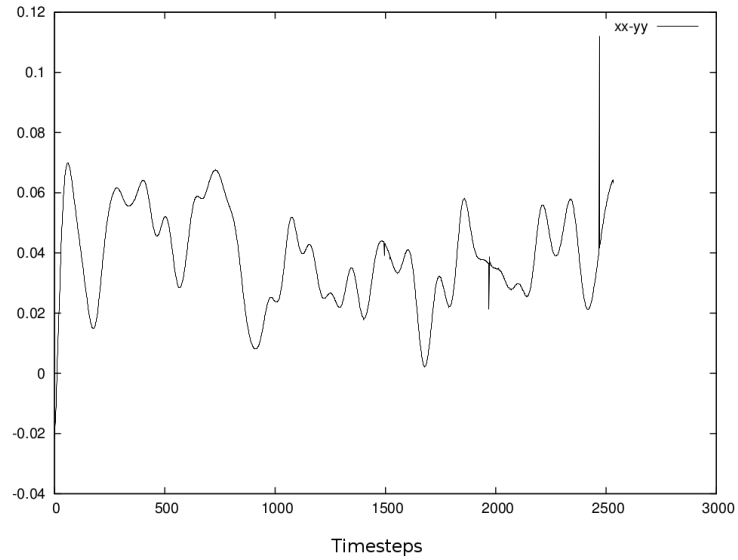


Figure 6: Normal stress difference over time of a mono-disperse suspension of bubbles with volume fraction $\phi = 0.14$ and Capillary number $Ca=0.16$.

and

$$\eta_{r,\infty} = (1 - \phi_b)^{5/3}$$

where ϕ_b the bubble volume fraction. Our results from the simulations match quite nicely with the results from the previous expressions.

References

- [1] H.M. Mader, E.W. Llewellyn, and S.P. Mueller. The rheology of two-phase magmas: A review and analysis. *Journal of Volcanology and Geothermal Research*, 257(0):135 – 158, 2013.