POLITECNICO DI TORINO

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Multiscale Modelling of Flowing Soft Matter: Copolymers and Emulsions

This PhD Thesis wants to explore the topic related to multiscale modelling simulations of flowing soft matter. A multiscale approach, meaning that both macro- and micro- scales are assessed, was used to overcome some limits related to the modelling of both complex mixtures for industrial and academic purposes. The term *flowing soft matter* refers to those products that are obtained by mixing two or more phases (miscible or immiscible, w/ or w/o surfactants), that flow as a response to the application of a reasonable shear stress. A fundamental aspect, when dealing with soft matter, is related to its rheology. Its viscosity becomes a fundamental element in the success of these products in the market. The rheological behavior is strongly influenced by the microscopical phases and structures that creates when components are mixed. Moreover, these structures can evolve, due to the presence of high shear regions that are created in mixing devices, that influence aggregation, shape changes and re-orientation of the aggregates. The capability of predicting both the final shape, the number and the polydispersity of these peculiar structures is required to advance in the predictive models that are nowadays used when dealing with reproducing the viscosity of soft matter. In particular, copolymers and emulsions, have been investigated using meso- and macro- modelling, keeping in mind that approaches and systems may be interchanged. Computer simulations have been performed on two different scales, i.e. mesoscale and macroscale, by using respectively *Dissipative Particle Dynamics* (DPD) and *Computational Fluid Dynamics* (CFD).

Copolymers, e.g. mixtures composed by tri-block copolymer (Pluronics L64, P104 and P85 by BASF) and water have been investigated in both equilibrium and non-equilibrium configurations using DPD, a mesoscale approach. In DPD, molecular identity is lost, and atoms, molecules and particles are clustered together to form entities that interact via bonded and non-bonded interactions. Equilibrium simulations, to reconstruct phase diagrams, were performed on LAMMPS for three different species of Pluronic. Results were validated against experimental evidences. The microstructures were qualitatively and, when possible, quantitatively validated by identifying their status of aggregation. In particular, when micelles and worm-like structures were present, their sphericity was calculated with an in-house developed clustering algorithm that is able to identify different clusters, calculate their gyration radius and how they evolve during the simulation time in response to shear stress. In Figure 1, it is possible to appreciate the different phases identified for a system composed by water and Pluronic L64, at different volume fraction of copolymer. Colors represent beads of water (blue) and Pluronic L64 chains (PEO: yellow, PPO: pink). It is possible to appreciate how spherical aggregates, at low concentration, evolve into worm-like structures,

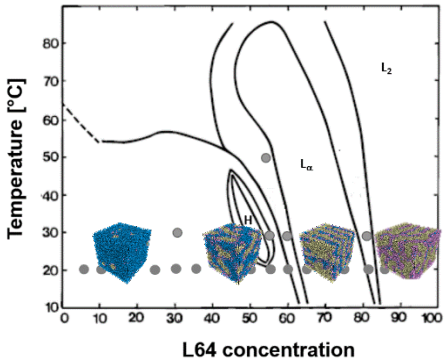

Figure 1 *- Pluronic L64 phase diagram: simulation boxes are compared against experimental results. Four phases (L_1: spherical micelles, H: hexagons, L_α: lamellae; L_2: reverse micelles). Ref. Temperature: 25°C.*

interconnected network, lamellae, and eventually reverse micelles when the volume fraction of copolymer increases. The interaction parameters that have been used to reproduce Pluronics L64 were also applied on the other two kinds, proving their scalability. This finding reduces the number of lab-scale experiments that needs to be performed in order to identify peculiar microstructures. Shear effects, e.g. because of the stirring, have been evaluated, at this scale, by looking at the modification of the microphases, such as coalescence, deformation, and alignment. In order to perform these simulations. Figure 2 shows the evolution of the viscosity of boxes of Pluronic L64 in water, at different concentrations of copolymer, and the morphological changes associated with this event.

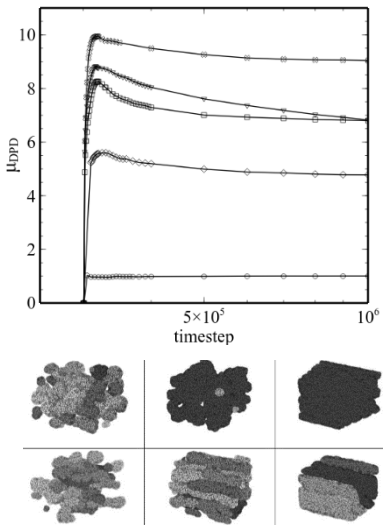

Figure 2 *– Top: Viscosity curves against simulation time for Pluronic L64/Water mixtures at different vol. frac (5% (●), 0.55% (◊), 75% (□), 80% (Δ), 85% (x)). Bottom: snapshots of the the system at 20% (left), 55% (mid), and 75% (right) in equilibrium (top) and non equilibrium (bottom) obtained via clustering algorithm.*

Attention was focused on the variation of the number of aggregates identified, their morphological changes, and the variation of the viscosity in time for all the range of concentration. Shear thinning behavior, observed between 40% and 65% vol. of Pluronic was confirmed with experimental tests, while Newtonian behavior lasts at low concentrations.

In the manufacturing process of soft matter, stirring is a fundamental operation. We reproduce the industrial mixing by using CFD. A stirred tank and an inline rotor-stator mixer were simulated by using the two-fluid model and population balance equation solved by the quadrature method of moments. Emulsions composed by of silicone-oil in water, at low volume fraction (1% vol.) and different viscosities in presence of surfactants were investigated on a full 3D scale, with in-house implementation of PBE and QMOM into Ansys Fluent. Figure 3 reports the CAD geometries used for the purpose.

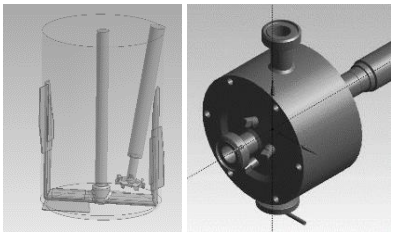

Figure 3 - CAD geometries of ESCO 6l (left) stirred tank, and Silverson (right) rotor-stator mixers used for manufacturing emulsions.

Multiple reference framework (MRF) was used to reproduce the stirring effect and results have been validated against the empirical correlations for the power number of these systems and experimental evolution of the droplet size distribution. In Figure 4, it is possible to observe the simulated power numbers for the Silverson mixer compared with the pilot-plant scale experimental law.

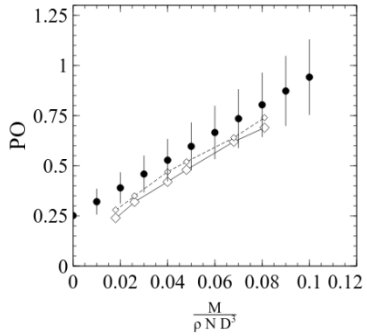

Figure 4 *- Experimental Silverson Mixer Power Number (●) compared against simulation results (◊). Only the final mesh has been reported, while two turbulence models (k-ε: solid line, k-ω: dashed line) are compared.*

Different meshes and turbulence models were tested in order to ensure grid independence. In figure 4, the axes represent the dimensionless flow rate (where M is the flowrate in kg s^{-1}, ρ the density of the continuous phase in kg m^{-3}, D the diameter of the impeller in m, and N the rotation speed in rev/sec) and PO is the power number, a characteristic number of the impellers.The same approach was used to validate the ESCO 6l mixer, by varying the turbulence model.

In order to obtain the evolution of droplet size distribution for all the silicone-oil-in-water mixtures, two kernels have been implemented in Fluent and tested to better describe the breakage phenomenon, while coalescence was turned off because of the presence of surfactant into the system. Figure 5 reports the evolution of the Sauter diameter of the droplets in time, for the different viscosities by using Laakkonen kernel. 3D models have been compared with 0D simulations in MATLAB, which provided similar results but in reduced computational times.

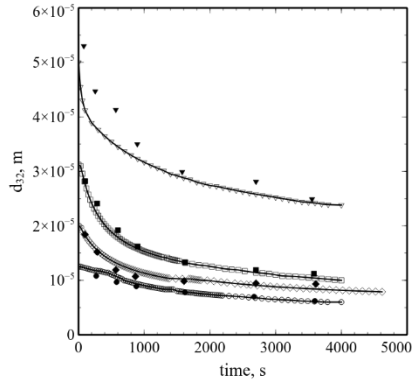

Figure 5 *– Sauter diameter of the droplets of silicone oil in water, obtained for four viscosities (0.5mPas (●), 12 mPas (◊), 32 mPas (□), 242 mPas (Δ)). ESCO experimental results (full symbols) have been validated against simulations (empty symbols).*

A tuning on the kernel parameters was needed due to the differences in the physics of the breakage phenomenon at high values of the viscosity.

In this work we explored the capabilities of computer simulations of assessing both the quasi-molecular and the macro scale, regarding the manufacturing of products related to home and personal care industries. It was proved that coupling simulations with experiments is a powerful tool that can be used to speed up and optimize industrial processes. This will reduce the gap of knowledge about the many aspects of soft matter, such as all those phenomena that can only be appreciated at molecular level. Eventually, it was developed an OpenFOAM solver (C++, CFD code, open source code), where CFD scale sends information, such as shear rate and concentration of components, to DPD scale and receives a feedback on the evolution of transport coefficients. However, the conversion between the values obtained from DPD and real quantities is still missing. In the future, this tool will allow 3D macroscale mulations where models are directly derived from mesoscale observations.