Molecular simulation techniques for sustainable technology and environmental applications: general overview and case studies

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In this work we present a general overview of the potentialities of molecular simulations techniques to study environmental-related problems, for different length and time scale characteristics. A general presentation of some common fields where these methods are employed is given; then, finally some topical case studies of our group are presented and examined.

1. State of the art

In the last two decades the interest of the scientific community about molecular simulation techniques for applications in various chemical engineering fields is increasing. At the same time, studies and applications about environmental fields gained more and more importance. Nowadays there is a huge interest in the enormous potentialities for discovering chemical properties, morphologies, and thermodynamics of various materials and processes for direct environmental applications (Charpentier, 2002).

Moreover, the rapid developments of hardware/software available tools allow scientists to expand the scope and complexity of the investigated systems: this allows to tackle real world, complex problems, which were previously computationally unaffordable.

Recently, new investigation possibilities are given by the link between quantum-mechanics simulations up to process simulations (finite element simulations). This is the so-called Multi (or Many) Scale Molecular Simulation: properties obtained from lower scale (in terms of time and length scale characteristics), may be used as input data for higher scale simulations (Figure 1); this powerful approach makes one able to theoretically simulate a complete system, from electrons behaviour to the entire process.
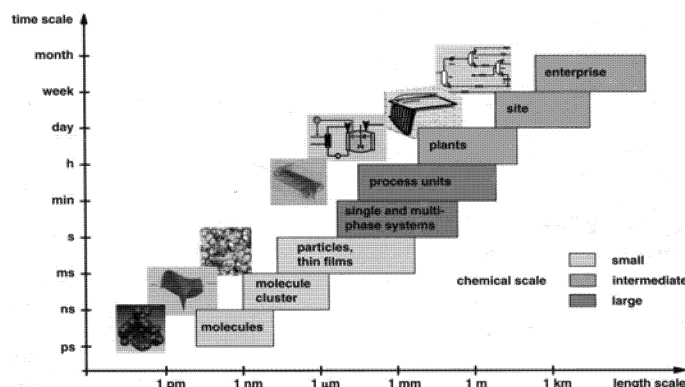
Figure 1: multiscale molecular modelling in terms of time and length for the different modules employed.

Molecular simulation techniques are nowadays used for property predictions, for processes customisation, or explore some useful insights of processes at low-scale level. Thus, it is easy to recognise how these techniques could be useful for environmental systems description: new insights at microscopic level of environmental processes, time and money savings by reducing experimental efforts, high repeatability of *in-silico* experiments, both for environmental phenomena description and for sustainable industrial process customisation.

To give only some examples of environmental applications, they can be used for testing and screening materials for contaminant removal (such as activated carbons, carbon nanotubes, zeolites, polymer membranes) both in aqueous and gaseous streams, and to select the optimal thermodynamic conditions of the process (Cosoli et al., 2007a), they can predict reaction rates in confined or unconfined (such as molecular sieves for adsorption) environments (Johnson et al., 1994) or even reaction kinetics (Turner et al., 2002). They can be used to predict preferential pathways, adhesion and diffusion of pollutant in specific environments, as soils, or water (Teppen et al., 1998). More, they are used for toxicity predictions of different classes of contaminants (Lin et al., 2003, Ren et al., 2003). Finally, they have some industrial interest for new materials property prediction, as, for instance, morphology, physical and mechanical properties of recycled wastes, such as polymers, polymer blends, nanocomposites, ceramics and metals (Cosoli et al., 2008b).

In this work we analyze the relatively unexplored potentialities of multi-scale molecular simulation techniques, and we show some case-studies of interest in different fields, which have been developed by our group. These include:

- studies of morphology, mechanical properties and compatibilisation of polymer blends and nanocomposites for industrial scraps recycling in the automotive field;
- simulated competitive adsorption of mixtures in microporous materials for pollutant removal;
- estimation of indicators (as water-octanol partition coefficients) which are useful to evaluate environmental impact categories.

2. Case studies

2.1 Automotive industrial scraps recycling

2.1.1 Tasks

The aim of the work was to investigate morphological and mechanical properties of polymeric materials to be used in the automotive field, as rear lamps for cars. There is an increasing interest about scrap recycling from industrial production of these materials. In fact, EU directive 2000/53 states that, before 2015, 95% of vehicle scraps have to be recovered, while 85% have to be recycled. Thus, we studied the possibility of mixing these scraps for reutilisation in a mixture analysing morphologies (miscibility) and mechanical properties (Young's modulus) of the blends. Scraps were mainly constituted by polycarbonate (PC), polymethylmetacrilate (PMMA) and Acrylonitrile (AN)-Butadene (B)-Styrene (S) blend (ABS).

2.1.2 Simulation techniques

Multi-scale simulation techniques have been employed, from quantum-mechanics to finite elements calculations. Quantum mechanics are used for charge and bond evaluation of single molecules. Atomistic simulations have been performed for the prediction of single polymer chain and blends behaviour. These input data are used for mesoscale simulations of polymeric blends, and then density distributions have been employed for calculations with Finite Element Methods (FEM) in order to predict mechanical properties.

We used the MesoDyn® simulation method, based upon the mean field density functional theory (Altevogt et al., 1999), to predict the phase behaviour of the blends. The mesoscale molecular model consists of beads of various types, each of which represents a group of monomers in the chains. The number of monomers contained in each bead depends on chain flexibility and is related to the polymer characteristic ratio C_{∞}, previously obtained by sets of atomistic simulations. The method relies mainly upon the determination of the Flory-Huggins parameters χ_{ij} which have also been obtained via atomistic simulations, by the calculation of solubility parameters δ_{ij} between polymer chains. Simulations results are given in terms of bead local densities; the so-called order parameters P_I, defined for each species I as the deviation from the mean bead density at homogeneity (Fermeglia et al., 2006). Order parameters with large values indicate strong phase segregation, while small values of P_I correspond to homogeneous systems. Density field distributions are then used for Mesoprop® FEM calculations (Gusev, 2001) to obtain macroscopic, mechanical properties, knowing the properties of pure components.

2.1.3 Results

Morphologies of ABS, PC/ABS, PC/PMMA/ABS blends are obtained at different temperatures and composition. As an example, in Figure 2a mesoscale density distributions of ABS at 280 °C (extrusion temperature) is shown; it can be seen how the most polar AN and PC beads are separated by the presence of S and B, that bridges between PC and AN to lower unfavorable interactions. In particular, we can also observe that there is a clear distinction between rigid and rubbery phases (islands of B), with PMMA in the middle. Then, in Figure 2b, the calculated Young's modulus for the blend is compared with the one obtained experimentally; PC fraction is constant (55%), PMMA and ABS fraction is variable. Thus, these results and the adopted procedure are

able to predict morphologies and mechanical properties of the recycled materials as a function of process characteristic and polymeric fractions.
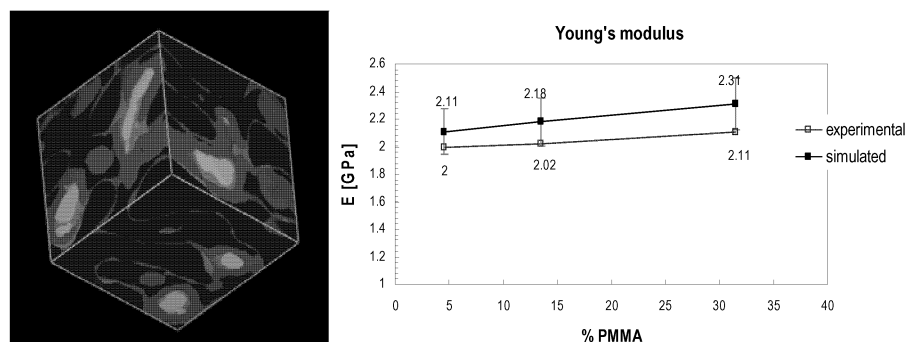

Figure 2: a (left), PC (55 %)-ABS (31.5 %)-PMMA (13.5 %) morphology at 280 K; from light gray to black: PC, PMMA, B, AN, S; b (right): experimental and calculated Young's modulus for the PC/PMMA/ABS blend as a function of PMMA fraction.

2.2 Competitive adsorption for pollutant removal

2.2.1 Tasks

Adsorption over porous materials is a frequently used method for mixture separation, as in the case of pollutant removal (Noll et al., 1991). In this case we examined adsorption isotherms for a prototype of a biogas stream, where H_2S is the pollutant to be removed. The aim was to choose the most suitable structure from a list of examined zeolite structures.

2.2.2 Simulation techniques

The work mainly relies upon the use of Grand Canonical Monte Carlo (GCMC) simulation techniques; adsorbed molecule construction requires also the use of quantum-mechanics and atomistic molecular mechanics and dynamics simulations. It is a stochastic, atomistic-based method (Metropolis et al., 1953), where simulations generate configurations of a system by making random changes to the positions of the present species, together with their orientation and conformations, where appropriate (Leach, 2001). The Grand Canonical Monte Carlo ensemble (GCMC), creates, destroys, translates, and rotates molecules in order to obtain thermodynamic equilibrium in an open system. A trial move is accepted if it lowers the configuration energy of the system. The system chemical potential μ, volume V, and temperature T are kept constant, as if the framework is in open contact with an infinite adsorbate reservoir at a given temperature; thus, the reservoir is described by temperature and fugacity (or partial pressure) of all components.

2.2.3 Results

Adsorption isotherms at a total pressure of 1 atm, and at a temperature of 298 K have been performed over hydrophilic zeolites FAU (NaY, Si/Al= 2.49, and NaX), LTA and hydrophobic, all-silica MFI, both for pure benzene and for mixtures, with a typical pressure composition of CO_2 40%, and CH_4 60%; while H_2S ranges from 10 to 1000 Pa (only few ppm). In Figure 3, adsorption isotherms are shown, while in Figure 4 H_2S selectivity towards CO_2 and CH_4 is presented. Considerably different behaviors for

adsorption isotherms of pure H_2S and for the biogas mixture are obtained. As expected, the adsorption of H_2S on the hydrophobic MFI network is always lower than all other zeolites; moreover, considerable differences (1 to 4 orders of magnitude) clearly allows to establish a ranking for zeolites to be chosen. This is even more clear examining selectivities. Selectivity factors are generally very high, both towards CH_4 and CO_2, in all hydrophilic zeolites; according to our simulation results, the best results are achieved with NaY.
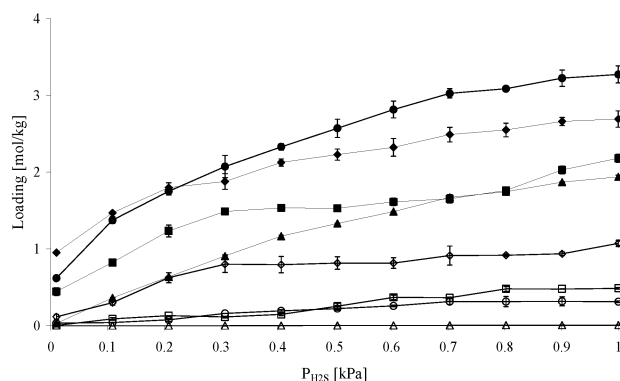

Figure 3: adsorption isotherms for pure H_2S) and H_2S in a biogas mixture. Pure H_2S simulations: (♦), NaY; (■), NaX; (●), LTA; (▲), MFI. Biogas mixture simulations: (◊), NaY; (□), NaX; (○), LTA; (△), MFI.
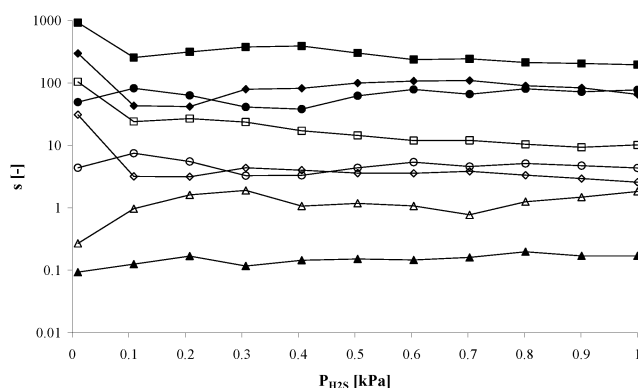

Figure 4: selectivity factor for H_2S with respect to CH_4 ($S_{H2S,CH4}$) (filled symbols) and to CO_2 ($S_{H2S,CO2}$) (open symbols). Symbols legend: (■, □), NaY; (●,○), NaX; (♦,◊), LTA; (▲,△), MFI.

2.3 Evaluation of octanol-water partition coefficient

2.3.1 Tasks

Toxicological data are usually necessary to assess the impact of such compounds on the environment and on human health. They can be obtained by performing appropriate toxicity tests (Ren et al., 2003). In recent years, octanol-water partition coefficient (Kow) has become a key parameter in studies of the environmental fate of organic

chemicals. The octanol-water partition coefficient is defined as the ratio of the concentration the component of interest has in octanol phase to its concentration in the aqueous phase in a two-phase octanol-water system (Lin et al., 2003).

Kow has been found to be related to water solubility, soil/sediment adsorption coefficients, and bioconcentration factors for aquatic life. Kow is considered a required property in studies of new or problematic chemicals (Ren et al., 2003; Lin et al., 2003). Kow is also used in the calculation of some environmental impact categories: Human Toxicity Potential by Ingestion, Human Toxicity Potential by either Inhalation or dermal Exposure, Aquatic Toxicity Potential and Terrestrial Toxicity Potential.

2.3.2 Simulation techniques

There are different molecular modelling methods to calculate the octanol-water partition coefficient. The results of two of these methods (QM-COSMO and QSAR), applied to some representative substance of industrial interest, are reported in the present paper.

QSAR is a mathematical model that relates a quantitative measure of chemical structure to a biological effect (Leach, 2001). QSAR is a common method used for the octanol-water partition coefficient. QSAR studies consist of two main stages. In the first step, the chemical compounds are described and drawn; afterwards the quantitative correlation between chemical structure and its chemical-physical properties can be obtained using different statistical and learning procedures, like multiple linear regression model, several types of artificial neural networks, partial least square method, etc. QSAR methods are very fast, thus they can be applied to large databases of structures, and they can be very accurate for classes of molecules with well-defined group equivalents. A disadvantage is the necessity of a large set of available experimental data. Thus, they perform well, but only for very narrow classes of compounds.

The COSMO method (Klamt and Eckert, 2002), based on computational quantum mechanics (QM), allows to predict different thermo-physical properties without any experimental data. The COSMO method contains two models: conductor like screening model-realistic solvation (COSMO-RS) and conductor like screening models-segment activity coefficient (COSMO-SAC). Basically, COSMO-RS method assumes that the molecule is made up of small surface elements. The charge density of each of these elements is evaluated by means of quantum mechanics calculations. An ensemble of interacting molecules is replaced by the corresponding ensemble of interacting surface pieces characterized by a screening charge density, namely, the contribution of all of the differences in polarity obtained when the molecules are not isolated. The characteristic distribution of charges obtained by considering all of these surface elements is the sigma profile (σ-profile) of the molecule. The sigma profile describes the amount of surface in the ensemble having a screening charge density between σ and $\sigma + \Delta\sigma$. Sigma profiles depict the surface charge density distribution over the entire molecule. It has to be specified that each molecule's profile is unique and the profiles are sensitive to conformation. The sigma profiles provide a rich and detailed quantitative information about the polarity of molecules. As a big advantage, each molecule is characterized by a sigma profile, so the method can treat proximity effects, can distinguish among isomers, and can also take into account the result of a conformational analysis (Fermeglia et al., 2006).

The above-presented methods for Kow calculation have been implemented in different software programs: COSMO-RS method has been implemented in COSMO*Therm* software and QSAR has been implemented in Estimation Programs Interface (EPI) Suite software developed by EPA (KowWIN™). It should be also specified that two software programs have been used in the present work to generate the sigma-profiles: TURBOMOLE and Accelerys' Materials Studio®.

2.3.3 Results

The results of QM-COSMO and QSAR methods applied to some representative substance of industrial interest are reported in Table 1. It can be noticed that the logKow relative absolute deviation (RAD) has lower values for nine substances when the quantum mechanics (QM-COSMO) method has been used for the logKow estimation. The mean relative absolute deviation (MRAD) has lower value (0.00765 vs. 0.10715) when the QM-COSMO method has been used for logKow calculations. Results show a good accuracy of the QM-COSMO method.

Table 1: Kow results using different methods.

Substance name	Substance formula	Substance CAS	logKow (exp.)	logKow CALCULATED		Kow RAD	
				(1) QSAR method KowWIN™	(2) QM COSMOTherm	RAD for (1)	RAD for (2)
Methanol	CH_4O	67-56-1	-0.77	-0.63	-0.7292	0.1818	0.0529
Naphthalene	$C_{10}H_8$	91-20-3	3.30	3.17	3.0939	0.0393	0.0625
Phenol	C_6H_6O	108-95-2	1.46	1.51	1.4319	-0.0342	0.0192
Chloroform	$CHCl_3$	67-66-3	1.97	1.52	2.1001	0.2284	-0.0660
Toluene	C_7H_8	108-88-3	2.73	2.54	2.6549	0.0696	0.0275
Anisole	C_7H_8O	100-66-3	2.11	2.07	2.2271	0.0189	-0.0555
Methyl Ethyl Chloride	CH_2Cl_2	75-09-2	1.25	1.34	1.2591	-0.0720	-0.0073
Benzene	C_6H_6	71-43-2	2.13	1.99	2.1043	0.0657	0.0121
Methane	CH_4	74-82-8	1.09	0.78	1.0162	0.2844	0.0677
Ethane	C_2H_6	74-84-0	1.81	1.32	1.6319	0.2707	0.0984
Propane	C_3H_8	74-98-6	2.36	1.81	2.1782	0.2330	0.0770
Benzoic Acid	$C_7H_6O_2$	65-85-0	1.87	1.87	2.2379	0	-0.1967
						MRAD	
						0.10715	0.00765

3. Conclusions

The case studies presented in this work, and the vaste literature about this fields, demonstrate that molecular simulation techniques are already reliable and robust. The examples cited above demonstrate how simulation techniques are nowadays mature as a

powerful, original tool to explore environmental problems and systems in a more deeper and detailed way, to give more insights of processes and physical-chemical phenomena at lower scale level.

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