Molecular Modeling of Transport Phenomena in Polymeric Membranes

by Elena Tocci, Emanuele Bellacchio

Molecular modeling represents a valid contribution in the studies of membrane systems. Computer aided experiments can in fact decrease time and cost of membrane preparations, and contribute to the understanding of the transport phenomena which originate selectivity and permeability.

In the last years, membrane science has achieved many progresses with a significantly high transfer of knowledge into practice. The availability of different kinds of dense materials, either inorganic or polymeric, has encouraged the realization of membrane devices able to carry out a huge variety of operations. Processes such as gas separation, cross-flow microfiltration, ultrafiltration, reverse osmosis, nanofiltration, pervaporation, electrodialysis and so on, are nowadays considered fundamental units in separation technology. Sea water desalination, industrial effluent treatments, food packing, encapsulation of electronic components in polymer able to block gaseous pollution, artificial organs in medicine, membranes in integrated systems for life in the space stations or inside submarines are only a few examples of possible applications in different technological sectors [1].

Among the several processes in which membranes can be implemented, high attention is paid to the feasibility of performing gas separations. In the last century, oxygen and nitrogen productions were established at industrial level by means of liquid air distillation. This process requires a high amount of energy in order to keep the operating temperatures in the distillation towers. As long a renewable source of energy will not be available, there is the need to redesign the processes that enable gas production and separation at a large scale with the requirement of low energetic cost. In addition to this, it is also necessary to limit enormously all the air pollution. This issue is challenging and the continuous progresses in membrane science are demonstrating how well these materials can be implemented in processes that require separations, purification, catalysis, selective permeation and so on. The nature of membrane based processes is such to require lower energetic aid, respect to other traditional means. However, in every technological application it is crucial to find materials with the desired properties. The establishment of quantitative relationships among material structure and function represents an area of strategic interest. Preparation of new membranes is often left to a trial and error method, very often highly expensive in terms of synthesis cost and time.

Computer simulations can provide an alternative and helpful procedure. With the methodological advances and increase of computational power, simulations are becoming a tool that laboratories must have rather than a nice-to-have option. For example, bioinformatic is gaining big benefits from molecular modeling; the field of drug discovery is developing rapidly because of the enhanced ability in building molecules that can interact as desired with biological active sites. Similarly, computational chemistry is becoming more and more used in designing and producing new membranes and also in predicting the corresponding transport properties [2].

The quantitative prediction of the behavior of materials requires accurate calculations with a high power of computational machinery and the physico-chemical knowledge in order to integrate computational methods with the experimental data.

Polymeric amorphous materials have been studied with a wide range of methodologies, ranging from continuum models to detailed atomistic ones [3,4].

By studying dense membranes with molecular dynamics (MD) simulations it is possible to obtain information of systems with size of the order of nanometers. The knowledge of the interatomic interactions can furnish fundamental mechanistic understanding of the material response to external forces.

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Membranes

Membranes are used in various molecular separation systems as interphases between two homogeneous or heterogeneous bulk phases, feed and permeate. Separation is achieved because the membrane has the ability to transport one or more components from the feed phase more readily than any other components under appropriate driving forces [5, 6].

In principle, all materials that form sufficiently thin films can be used as membranes. For this reason all materials have been classified on the basis of nature (natural or synthetic), of structure (asymmetric or symmetric), of surface (dense homogeneous or porous), of physico-chemical properties (idrophobic or idrophilic), of separation mechanism (molecular sieving, solution-diffusion, etc.) [5].

The transport process through a membrane is driven by a difference in the chemical potential and permeation mechanism is controlled by a gradient of pressure, concentration, temperature or from the combination of more than one of these variables.

Polymers are the materials more frequently used today in the preparation of commercial synthetic membranes in gases separations. The reason lies in the high potentiality in term of selectivity respect to different type of gases: when a gas or a volatile species is let in a polymeric material, it interacts more or less with it in a manner depending on the type of chemical groups and topology of structures.

A thermodynamic factor, solubility, and a kinetic diffusion process controls the permeation mechanism in dense polymeric membranes for separation in reverse osmosis, pervaporation and gas separations. In particular the passage of gases can be seen as a “solution-diffusion” process, a three step mechanism which includes absorption, diffusion and release of gases through the membrane (Figure 1).

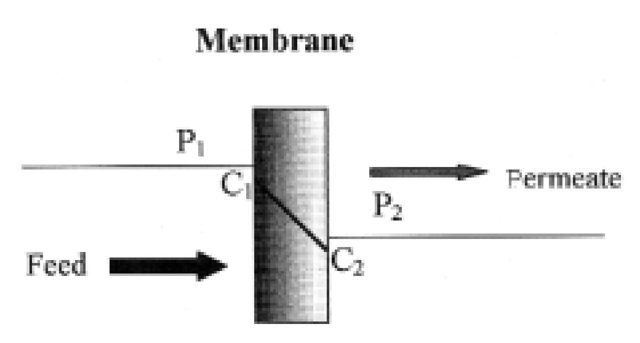

Figure 1 - Concentration profile across membrane

The rate-determining parameter is the permeability coefficient, P, that can be factored into diffusion, D, and solubility, S, coefficients as follows:

$$P = D \cdot S \tag{1}$$

Permeation through dense polymeric membranes has been extensively described in literature using several concepts such as the free volume of the polymeric matrix, statistical and energetic considerations [7].

At a microscopic level the diffusion can be calculated as time integral of auto-correlation function (Green-Kubo relations) being a measure of how long an atom will continue in a given direction before this direction is randomised or reversed.

$$D = \frac{1}{3}\int_0^\infty \langle \mathbf{v}(t)\mathbf{v}(0)\rangle dt \tag{2}$$

The Einstein equation, which assumes that the motion of a particle follows a random walk at long-time limit, is equivalent to the equation (2).

$$6Dt = \left\langle \left|\mathbf{R}(t) - \mathbf{R}(0)\right|^2 \right\rangle \tag{3}$$

In this case the diffusion coefficient involves the atomic mean-square displacement *(msd).*

If particles diffuse in a right way the *msd* is linear in time but there exists other mode of motion. In the case of shorter time the motion of *msd* may not be random but may depend on the environment restricting the particle into a certain conformation to diffuse through polymer chains.

In most of the polymers studied so far, especially in gas separation, an increase in permeability implies a decrease of selectivity. However suppressing the interchain packing and inhibiting interchain motion due to the inclusion of bulky groups into the backbone can improve membrane selectivity and then overall performances.

The related diffusion coefficients are completely determined by the jump event. The presence of cavities connected by channels with dimensions comparable to those of the gas molecules increases the time of residence inside the solid. Light differences in the physical properties of the gases (size, geometry, polarity and polarizability) can lead to different interaction gas-solid matrix. Hence, with the choice of particular materials having suitable structural features, better selectivity in the separation of gas mixtures can be achieved. The same principle can be applied to removal of undesired volatile species, i.e. low cost materials can be also designed for the trapping of toxic volatile substances coming from industrial or transportation exhausts.

Despite these interesting premises, it is currently impossible to determine experimentally the detailed interactions at atomistic level between gas and polymer, which indeed is critical for the understanding and optimization of processes. An attempt to improve the selectivity would be best carried out when it is possible to characterize the spatial arrangement of the polymer backbone and side chains. Only the knowledge of the geometric features of the cavities and channels inside the polymer can allow the understanding of the mechanics of interaction between gas and the solid phase, allowing thus the design of better materials.

Recent progresses in membrane research

A number of Molecular Dynamics (MD) and Monte Carlo (MC) simulations of diffusion of small molecules in amorphous and semicristalline polymers appeared in the scientific literature [2, 8, 9]. Most of these simulations deal with gas diffusion in the bulk of flexible chain polymers composed of rather simple monomers like PDMS, poly(isobutylene), poly(ethylene) and poly(propylene) [10-23]. Few papers on MD simulations on stiff chain polymers are reported [24-27].

It must be pointed out that because a MD simulation can involve only few thousands of atoms, the maximum size of the simulated system is severely limited and might not include all the processes occurring in a macroscopic membrane. However, it is still possible to solve the problem by breaking the system under examination in more parts, and describing the specific phenomenon occurring within each of them. For example in the work of Hofmann *et al.* [2] pervaporation through membranes is described as individual processes occurring separately in the bulk and at the interface of the dense material: the bulk-model examines the diffusion inside the body of the membrane, while the interface-model treats the adsorption (or desorption) of different liquid mixtures at the interface between feed (or permeate) side and the polymer membrane surface.

PDMS (hydrophobic) and PVA (hydrophilic) have been used for the enrichment of ethanol from water/ethanol mixtures. The use of the first membrane becomes optimal in case of water/ethanol mixtures with low ethanol load, when this organic specie can be transported with higher speed into the permeate side, and collected there as enriched component; on the other hand, the hydrophilic membrane is more convenient for water/ethanol mixtures, where the ethanol load is higher: in this case, water molecules cross the membrane at higher speed, being preferentially expelled in the permeate side, while the feed content becomes enriched in ethanol.

The parameters that characterize gas permeation processes inside membranes need to be validated by the experimental results. There is a number of works where the calculated diffusion coefficients are in a relatively good agreement with the experimental ones. In Tocci *et al*. [28], the diffusion of hydrogen, nitrogen and oxygen through cardo poly (ether-ether-ketones)s, PEEK-WC, has been examined. The theoretical values obtained by MD simulations are acceptably close to the experimental ones. In addition, the sorption isotherm of carbon dioxide was also simulated and successfully validated with the experiments. It is worth to mention that from this kind of calculations it is possible to better characterize the effect of change in the rigidity of the chains. There are consistent results that show how polymers with stiff chains are characterized by low permeability values in comparison with more flexible polymers. According to the mechanisms of gas permeation and polymer chain motions enlightened by MD simulations, this might be due to an higher probability of channel formations within the matrix structure. Gas molecules can in fact jump between adjacent cavities only when channels connect them. For example, since the PEEK-WC has a relatively rigid structure, as compared to polyimides and PDMS, the channels in the first polymer are found to last longer respect to the second. This increases the possibility of back jumps of the penetrants in the more rigid matrix, with, as a consequence, a slower averaged gas motion.

Once the effect of detailed mechanistic motions are known, it is more productive to perform experiments with intentional structural modifications. In the work of Charati and Stern [29] it is examined the passage of helium, oxygen, nitrogen, carbon dioxide and methane through four silicon polymers with the size of the side chain increasing in the following order: poly(dimethylsiloxane) (PDMS), poly(propylmethylsiloxane), poly(trifluoropropylmethylsiloxane) and poly(phenilmethylsiloxane). The glass-transition temperature, T_g, increases in the same order, suggesting slower chain motions, and as expected, the diffusion coefficients calculated for all the four gases decreased accordingly. In addition, the calculated permeation rates for all the four polymers decreased regularly going towards larger penetrants.

Singh and Koros [30] have explained how the small geometric differences between nitrogen and oxygen could be discriminated by materials like zeolites and carbon molecular sieves. In particular, it has been argued for the steric restrictions imposed by the small cavities of these materials which limit the rotational degrees of freedom of gases in the diffusional activated states. The slower speed of nitrogen respect to oxygen within these materials is, in this optic, attributed to the longer shape of the first gas. Zimmermann and Koros [31] designed gas separation experiments employing a series of hyperrigid polypyrrolone copolymers with the aim to achieve entropic selectivity comparable to that obtained in zeolites or carbon nanotubes.

The transport properties across membranes are dictated by the intrinsic nature of the material itself, by characteristic packing and spatial arrangements of polymer backbone and side chains. However, there are different way to modify these structural characteristic. While it is very interesting to look for new polymers with premeditated and new designs, another feature that must be kept in mind is the fact that even relatively rigid materials have indeed dynamic properties, and are susceptible to potentially useful modifications upon combination with chemical agents. New materials can in fact be made either with new pathways in polymer chemistry or introducing some other components to already known polymers. For example in Samus and Rossi [32], the authors have examined the differences in the diffusion behaviors in ethylene-vinyl alcohol copolymers, upon exposure to various amount of methanol as plasticizing agent. The diffusion coefficients are dramatically dependent on the physical state of the polymer, showing low values in the glassy state and high values after plasticization. An interesting way to transport gases through membranes with very high selectivity is the one achieved by ion-conducting materials: solid oxides are used for oxygen transport, while proton exchange materials (either polymeric or inorganic) are used for hydrogen transport [33].

Molecular Dynamics

The dynamical behavior of penetrants in polymeric membranes can be investigated by performing molecular dynamics (MD) simulations. The motion of the nuclei can be treated, in its simplest form, classically solving the Newton's equation of motion:

$$\mathrm{m}_i \frac{d^2\mathbf{R}_i}{dt^2} = F_i = -\nabla_i E(\mathbf{R}) \tag{4}$$

where R_i denotes the nuclear coordinates, m_i its mass, F_i the force acting on atom *i* and E(R) the potential function. This differential equation is subject to the initial conditions and to suitable boundary conditions, using an integration algorithm. The initial conditions in a molecular simulation are the positions and the velocities of all atoms. The initial velocities are picked randomly from a Maxwell-Boltzmann velocity distribution at the chosen temperature; for amorphous polymer well "equilibrated" structures are taken as starting position. Periodic boundary conditions are used to mimic bulk behaviour: the original system is surrounded with an infinite number of copies of itself in all dimensions, and if one atom leaves the parent cell its periodic image appears at the opposite side.

The force given by the gradient of the energy E(R), depends on all nuclear coordinates R_i and is often described by parametrized interatomic potentials with parameters adjusted to experimental data. Lattice constants, positions, bulk modulus, frequencies, are experimentally available around the equilibrium geometry, and, thus, such parameters can be adjusted to reproduce them. A typical force field for a polymeric system includes, using appropriate mathematics, deformations from equilibrium, in bond length, bond angle, dihedral angles and nonbonded interactions (considering Lennard-Jones and Coulomb potentials):

$$E(\mathbf{R}) = \sum_{bond} \text{length deformations} + \sum_{angles} \text{angle deformation} + \sum_{dihedral} \text{dihedral deformation} + \sum_{at\,om\ pairs} \text{non bond interactions} \qquad (5)$$

The analytical representations of the potential surfaces are called force-fields. The choice of the forms depend on several software now available. From the resulting atomic trajectories, one can obtain the atomic equilibrium structures, vibrations, etc. Systems may contain up to 10^4 atoms, and a simulation may last up to a few nanoseconds.

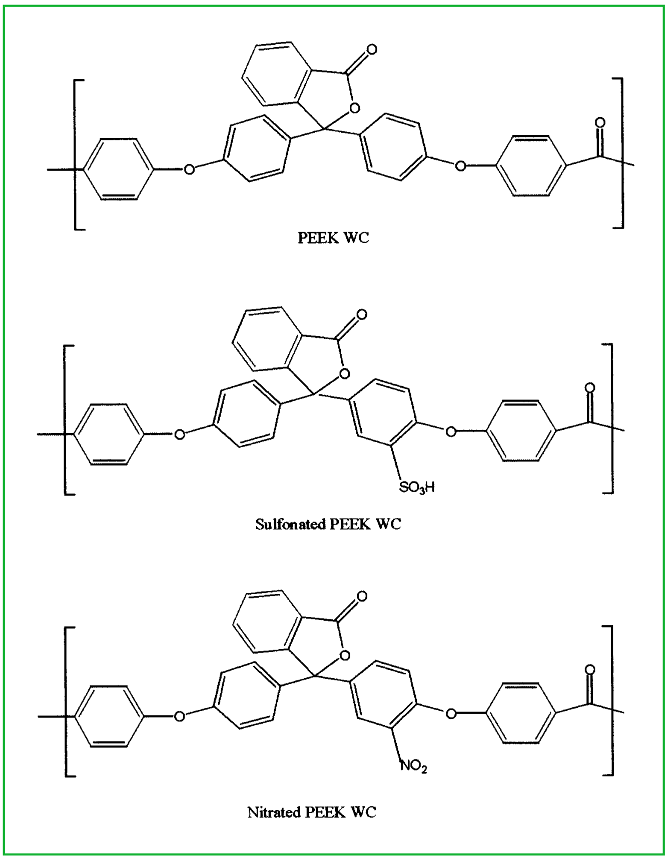

Figure 2 - Repeat units of some PEEK studied

Figure 2 shows the repeat units of some models studied by authors. Polymer bulk structures are generally cubic cells of few nanometers. Starting structure are grown with the Polymerizer and Amorphous Cell modules of the MSI, which implement a modification of the rotational isomeric state (RIS) method of Theodorou and Suter [34, 35]. The polymer chain is constructed at 303 K under cubic periodic boundary conditions; to have chain effects reduced, only one long chain, containing about 3000-4000 atoms, instead of several shorter chains segments, fills each simulation box. This procedure is chosen to come closer to reality where polymer chains are typically composed of at least several thousand atoms. After all packing and equilibration stages penetrants or bio-molecules are inserted during this stage into separated locations of the unit cell. The generation of an initial polymer structure is based on the "self-avoiding" random walk method of Theodorou and Suter: this means that for building the initial polymer structure resembling the equilibrium structure as much as possible, the correct statistics for the dihedral angles of polymer chain conformations had to be reproduced.

To avoid packing algorithm related catenations and spearings of aromatic units, that could appear in the first stage of packing production, it is necessary to start at a very low density. The experimental density is reached by increasing the pressure with several cycles of NPT (constant particle number, temperature and pressure) runs at pressures of thousands of bars and simulated annealing runs with temperatures up to 1000 K. The equilibrated packing models are then subjected to NVT-MD data and production runs at real density (Figure 3).

Diffusion through the rigid polymeric matrix

The information offered from MD simulations refers firstly to the direct visualization of the diffusion of molecules through the matrix investigating their path across the rigid membranes [2, 9].

In Figure 3 is shown the typical trace of oxygen and nitrogen molecules diffusing in poly(ether-ether-ketone) (PEEK-WC). The figure gives a clear idea of what happens microscopically when gas molecules move into the bulk of polymers. For certain periods of time the molecules reside in small regions of space exploring some cavities. In glassy polymers the penetrants spend most of the time in the same free volume regions of the polymeric matrix. The thermal fluctuations of the polymer matrix allow the formation of connections between adjacent voids. Only when a channel is formed, the gas molecules shift in very short time to the other void by hopping movements.

The intracavity hops do not contribute to the overall diffusion of the penetrant, in contrast the jumps between individual holes in the free volume areas determine the diffusive trajectory following the assumption of a random walk, i.e., the particle that diffuse has no memory of previous steps and the motion at some time is completely uncorrelated with its motion at any previous time. This behavior has been generally observed when gas molecules move into amorphous polymers [2,9].

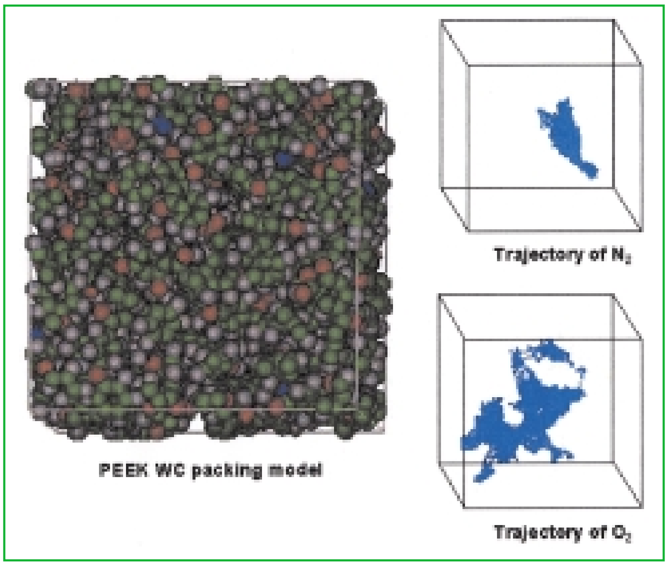

Figure 3 - Packing model of PEEK-WC and diffusion paths for oxygen and nitrogen molecules

In some cases the so-called anomalous diffusion, firstly discovered by Mueller-Plathe [18] consisting on restrictions of motion of particle due to the rigid environment of the structure, become visible in the low timescale range, preventing the molecule to perform the random walk.

The still rather short possible timescale of completely atomistic MD simulations (up to 10 ns) in many other cases results in a non-negligible influence of the very fast movement of penetrant molecules (timescale several hundred ps) inside the individual holes on the diffusion trajectories. This in-hole motion is determined by the shape of the holes and is therefore no random walk

Additionally the diffusion processes can be directly identified in plots of the displacements

$$|R(t)| = \sqrt{|r(t) - r(0)|^2}$$

of a penetrant molecule from its initial position r(0) as a function of the simulation time like Figure 4 where an hydrogen molecule is shown in the simulation box of sulfonated PEEK-WC. The particles move oscillating in a spatial range of few Angstroms that means in the same void for hundreds of picoseconds (ps). The amplitude of the oscillations depends on the size of the visited hole. From time to time larger oscillations (of about 10-15 Å) can be related to jumps into an adjacent hole. These jumps take only a few ps to occur.

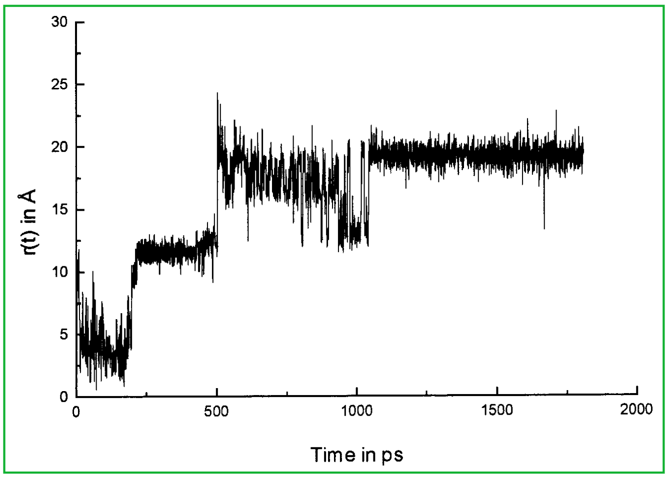

Figure 4 - Displacement |R(t)| of a penetrant H_2 molecule from its origin in the sulfonated PEEK-WC model

MD methodology helps usefully to have a closer look at the free volume of the packing models. Diffusion is related to the physicochemical properties of the polymeric matrix such as the fractional free volume determined by interchain packing and the stiffness of polymer backbone (which is also related to the glass transition temperature, T_g). Some authors like Singh and Koros [30] hypothesised that polymers loose entropic selectivity because penetrants have significant rotational freedom in the hopping event due the relatively large thermal motion of the polymer chains althougth recent theoretical studies [36] focused the effects of matrix flexibility on the entropic and energetic selectivities in glassy polymer. The results show that energetic selectivity is correlated with the rigidity of the structure nevertheless the entropic selectivity does not depend directly from stiffness but from dimension of cavities hinting that material design effort have to be directed toward the production of larger free volume regions into the polymeric matrix. It becomes quite interesting to analyze in details the distribution of holes into the bulk and the changes during the formation of channel between adjacent holes. The most simple way is to consider the small permeating molecules as probes of the free volume as shown in Figure 5. The picture shows the movement of an oxygen molecule through the polymer matrix in PEEK-WC [23] during a jump event. For this purpose, one suited slice of a thickness of 3.5 Å was cut perpendicular to the x-axis through the model. The slices are displayed at different simulation times between t=385 ps and t=389 ps. It is possible to observe that in cooperation with the displacement of the gas molecule along the polymer, temporary fluctuations of the matrix connected with the formation of a channel between two adjacent holes are evident. These thermal fluctuations are, however, less remarkable than for flexible polymer chains and also for polyimides and PDMS [2].

A more systematic free volume probing exists on the basis of the Gusev-Suter transition state theory [37-40]. The method permits estimation of diffusion and solubility constants of small gas molecules assuming that the polymeric matrix has only to undergo elastic fluctuations to accommodate the guest molecules.

In the Gusev-Suter method a three dimensional grid is layered over a completely equilibrated amorphous array. Then, inserting a gas probe molecule on each position of the grid the interaction energy between the gas molecule and all host atoms was calculated using a Lennard-Jones function.

Using these energy values the whole packing cell was separated in regions of free volume with low energy and regions of densely packed polymer with high interaction energy.

Figure 6 contains free volume maps obtained in this way for sulfonated and nitrated PEEK-WC. In both cases an oxygen molecules is used as probe molecule. The modification of the backbone chain of the original PEEK-WC results in a

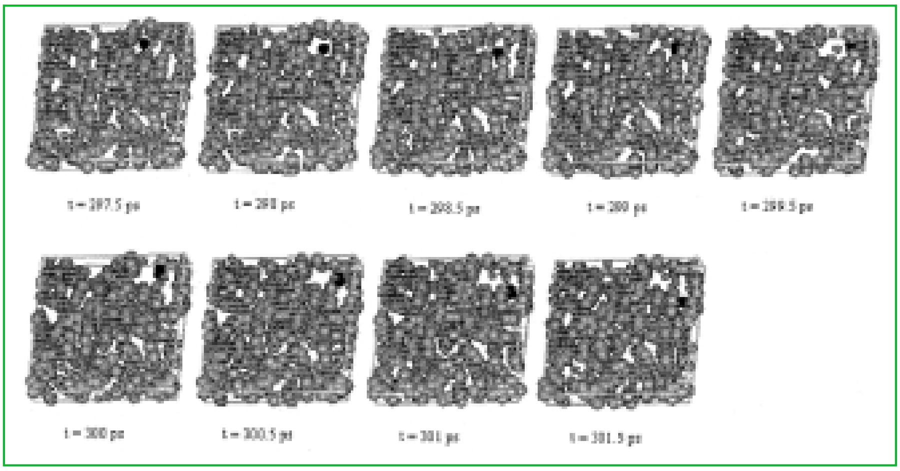

Figure 5 - Representation of a jump event in the PEEK WC: the 3.5 Å slices cut at different simulation times between t=385 ps and t=389 ps. The black coloured molecule indicates the oxygen and the grey represents the polymer matrix

bigger amount of voids available to be visited by gas molecules that generally results in greater permeability values. An interesting comparison is done between poly(ether-ether-ketone)s and perfluoropolymers showing that the latter material has holes interconnected to each other by channels of the dimension of some Angstrom resulting in a high permeability membrane [28].

Other interesting potentialities are offered by MD simulations applied on the study of membranes with catalytic properties like membranes filled with cyclodextrins (CDs) that are cyclic oligomers of α-1,4 linked *D*-glucopyranose. The main feature of CDs is an hydrophobic cavity which makes these molecule of great interest to a wide range of scientists in most of chemistry fields [41]. Together with their ability to host and to recognise substrates, CDs are able to catalyze some chemical reactions. In recent years the molecular modelling approach has been used to describe both the inclusion process and the structural features of cyclodextrins [42-51]. Our interest on these kind of system relies on the increasing studies of bioreactors composed of membrane supporting cyclodextrins, with both separation and catalytic properties [50]. Also a preliminary MD simulation, for the analysis of a wider project on non-bonding interactions and enantiomeric recognition, of octiloxycarbonyl β-cyclodextrins (β-CD) in glassy PEEK-WC material has been done showing that the mobility of β-CDs is reduced in view of the functionalized side chain group and of the rigid environment of bulk polymer [51].

β-CDs in PEEK-WC results slightly distorted [51] although this effect does not modifies the possibility of inclusion of guest molecules. More important seems to be the disposition of side chain that are immersed into the polymer matrix randomly, and in some cases inserted into the CD's cavity. This effect could influence the catalytic behaviour of CD's due to the hindering of the cavity that avoids the guest inclusion.

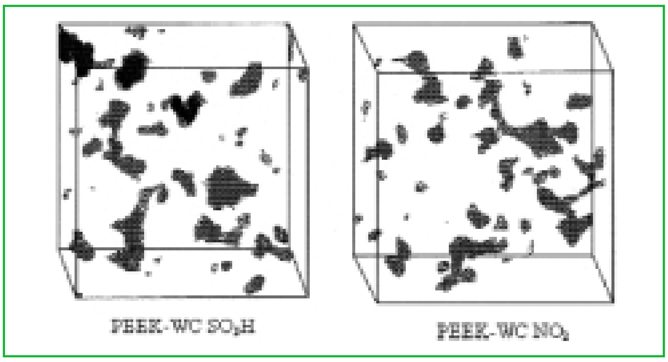

Figure 6 - Free volume maps obtained with the Gusev - Suter method of sulfonated and nitrated PEEK using oxygen as probe molecule

Conclusions

Computer simulation studies of dense membranes with molecular dynamics (MD) simulations have undergone a remarkable development over the past few years.

Detailed molecular dynamics simulations have become a widely used method for the investigation of the molecular structure of amorphous polymers and of the diffusion and solubility of molecules through these materials. Thanks to these methods, we can be obtain informations which would not be accessible by experimental means.

In the next years the scientific and industrial community will increase considerably the use of modelling methodologies to amplify the spectrum of membrane materials and membrane processes, implying also a development of molecule modelling methodologies.

Acknowledgements

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