

## The Free Volume in a Polymer Water Mixture

S. Capponi<sup>1,2</sup>, F. Alvarez<sup>3,4</sup>, D. Račko<sup>5,\*</sup>



(1) Department of Industrial and Applied Genomics, IBM Almaden Research Center, San Jose, California 95120-6099, United States. (2) NSF Center for Cellular Construction, University of California, San Francisco, San Francisco, California 94115, United States. (3) Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain. (4) Materials Physics Center, Centro de Física de Materiales, Apartado 1072, 20080 San Sebastián, Spain. (5) Polymer Institute, The Slovak Academy of Sciences, 84236 Bratislava, Slovak Republic. (\* dusan\_racko@savba.sk)

In this contribution we analyze the free-volume structure of a water mixture of poly (vinyl methylether) (PVME) on a series of trajectories obtained by molecular dynamic simulations. The structures with a water content equal to wt = 30% are analyzed in a wide temperature range between 300-175 K. The computed free volume is attributed to belong to a polymeric or water phases or to an interface between them, based on the environment of the free volume cavities. The basic free volume measures, like the cavity number, cavity volume, free volume fractions and the cavity distributions are evaluated and



discussed. The asymmetries between the water and polymer phases are discussed in terms of the free volume evaluations. The hydrogen bonding features in polymer and water phases are addressed as well.









will reduce the cavity sizes.

Figure 4 shows dependence of the cavity number related to the box volume. The computed cavity numbers are higher than those of the pure PVME by ~25%. This observation is consistent with the expected effect of the smaller water molecules, creating larger number of smaller holes.

observe a pre-peak, which belongs probably to some interstitial cavities observed also in simulations on the pure PVME.

Interphase

90.9 %

**58.4** %

854.6

Figure 8 shows distributions of the free volume associated with a particular molecular body – a polymer segment or a water molecule. In the case of the polymer segment the surrounding free volume was computed separately for polymer ends and for monomers. In the computation, when a cavity was already associated with a polymer end, 100 monomers sharing this cavity were not accounted in the evaluations. The distribution for polymer ends is more noisy with respect to monomers due to the lower statistics. However, no considerable

differences can be distinguished. The reason can be, that the contribution of the polymer ends is hidden in the contribution of the water molecules.

A particular feature of the PVME+WATER mixture is formation of a complex network of the hydrogen bonds between water molecules and polymer, and between water molecules themselves. The hydrogen bonds affect the mobility of the constituents in the opposite way than the free volume – by slowing the dynamics and restricting movements. This feature, however, should be somehow reflected also in the free volume. Here, we investigated this presumption by evaluating the free volume around molecular bodies (water molecules or monomers) with a given multiplicity of hydrogen bonds. Figure 9 shows, that multiplicity of the hydrogen bonds tends to reduce the free volume around molecules, hence having blocking effect on the constituents mobility.

Figure 10 shows a visualization of the hydrogen bonding network. The hydrogen bonds between water molecules themselves are shown in blue. The fraction of the watery hydrogen bonds is 82.9 %. Maximum multiplicity encountered is 3. Red sticks represent the hydrogen bonds between water and polymer.

In the molecular systems with higher specific volume, the free volume structure, obtained by probing with small probes can occur in larger cavities percolated by tiny bottlenecks and pathways. The larger quasi cavities, or "sub-cavities", can be distinguished by employing probes with larger radii within an additional free volume analysis. The bulk of the percolated cavity, corresponding to the o-PS probe is then reassembled around the closest sub-cavities.



Finally, the cavities are re-aligned from the simulation box with the periodic boundary condition, so that parts of the cavities, which cross the boundaries are put together. Then the analyses of environment and geometry of particular cavities starts.



vities

Figure 5

Figure 6

*Probe radius* [Å]



*Cavity volume* [Å<sup>3</sup>]

Figure 5 shows a different view on the data presented in the previous figure. Now the cavity numbers computed for different temperatures are shown as a function of the probe radius. We can see that the maxima of the cavity number is larger 1.50 at lower temperatures (175 K), and decreases as the structure opens and more molecular volume is accessible to the volume of a probe. In addition, the positions of maxima of the cavity number shift to higher probe radii with the increasing temperature. At these maxima the percolated structure breaks into individual cavities, so at higher temperatures larger cavities are expected. The position of the cavity number maximum computed for the **PVME+WATER** mixture at 250 K is roughly the same as observed for the pure PVME.

Figure 6 illustrates the free volume percolations. This figure shows the integral distributions of the free volume computed for the probe with the radius of 0.8 Å. The probe with this radius effectively determines individual cavities. At 250 K for the same probe an onset of percolation is encountered. At 300 K, for the probe of 0.8 Å most of the free volume (>90%) is localized in a percolated cavity.



Figures 10 (above) /11 (below)

Figure 11 visualizes the slices through the investigated structures. White regions are polymer segments, water molecules are red and the free volume structure is shown in a grey scale.



## References

[1] D. Račko, S. Capponi, F. Alvarez, J. Colmenero and J. Bartoš, J. Chem Phys, 131, 064903, 2009 [2] D. Račko, S. Capponi, F. Alvarez, J. Colmenero, J. Chem. Phys 134, 044512 (2011) [3] S. Capponi, F. Alvarez, D. Račko, Macromolecules, 53, 12, 4770–4782 (2020).

D.R. acknowledges support by the Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic, Grant VEGA 2/0102/20, and support is alsoacknowledged from the Slovak Research and DevelopmentAgency, Grants SRDA 16 0369 and SRDA 15 0323.