Free and Accessible Volume of Small Penetrants in a Poly(methyl methacrylate)-Carbon Nanotube Nanocomposite, via Monte Carlo integration

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ABSTRACT

Molecular simulations are employed to address water mobility in single-walled carbon nanotube (CNT) membranes based on atactic poly(methyl methacrylate) (aPMMA). Recent studies[1-3] in our group have shown that PMMA chains can significantly penetrate nanotubes through their faces and thus block their entrances, which can dramatically decrease the diffusivity of relatively small penetrants (such as water) in the nanocomposite membrane. According to detailed molecular dynamics (MD) simulations,[2] the escape time of a confined water molecule from the blocked mouths of a CNT can exceed by several orders of magnitude the time needed by the same molecule to move through the CNT pore. These past simulation efforts have also helped us analyze in detail how PMMA chains organize themselves both axially and normal to the CNT surface, and quantify their adsorbed conformations by distinguishing between trains, loops and tails.[1]

Here we further extend these studies by applying Delaunay tessellation followed by Monte Carlo integration to determine the clusters of sites where a hard-sphere penetrant (e.g., water) can reside in such a nanocomposite membrane, and analyze the dependence on penetrant size and temperature. By accounting for the volume occupied by polymer or CNT atoms, we provide estimates of the unoccupied volume as well as of the volume accessible to the spherical penetrant as a function of its radius within each tetrahedron. Interestingly enough, the total unoccupied volume fraction is found to be larger in the pure PMMA than in its CNT nanocomposites. It is only for very thin CNTs (so that PMMA chain penetration is totally avoided) that the total volume fraction accessible to water molecules is considerably larger compared to the pure PMMA matrix. Our work predicts also the volume distribution and the size of the cavities accessible to the penetrant. We find only a small number of large cavities in the PMMA domains of the nanocomposite, and most of which away from CNTs. A cluster connectivity analysis using the connectivity protocol proposed by Greenfield and Theodorou reveals that when PMMA chains penetrate CNTs, the total accessible volume fraction available to a penetrant molecule such as water becomes infinitesimally small.

Our work emphasizes the need to completely avoid (or at least minimize) penetration of polymer chains in the CNT pores through their mouths in enabling the efficient transport of small- to moderate-size molecules in model CNT-based polymer membranes, as this provides the highest resistance to their flow through the membrane.

REFERENCES

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