Multiscale Modelling of SIBS and sulfonated SIBS Copolymers

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Introduction

An important class of thermoplastic elastomers involves polystyrene and polyisobutylene blocks (SIBS). Sulfonated SIBS Triblock Copolymers (S-SIBS) are of particular interest because of potential applications for fuel cell and textile applications, where breathable, protective clothing is required. We have used multiscale modeling to gain an understanding of the static and dynamic properties of these polymer systems at detailed atomistic and mesoscale levels.

Results and Discussion

We first applied Quantum chemistry tools to elucidate the bonding of water molecules and sulfonate groups. It was found that a minimum of 3 water molecules per every sulfonated group are needed to spontaneously abstract a proton from the sulfonated group. If the sulfonated groups are present on neighboring styrene rings, the internal hydrogen bond stabilizes the acidic form of the group making proton dissociation more difficult. The quantum chemistry tools, also, allow us to validate the force field used and to rationalize an atomistic model for the next step of multiscale modeling - molecular dynamics. Molecular Dynamics was applied to calculate the polymer density at various levels of sulfonation and water content and in the presence of Zn, Ca, Mg and Ba ions. The structure of the acidic polymer neutralized with cations was studied in the presence of alcohols and water. Morphological channels allowing for diffusion have been identified. The self diffusion coefficients were calculated and compared to experimental data. The polymer density was reproduced with an accuracy of +/- 5%, while the diffusion coefficients calculated followed closely those obtained from the experimental results, although they obviously are highly dependent on the water and alcohol content. Both alcohols and water form a continuous network of hydrogen-bonded molecules linked to the sulfonated groups with a random distribution with respect to the isobutylene groups. The presence of metal counter ions slows down diffusion due to the stronger interaction with water molecules. The continuous percolation channel defined as surface accessible to water was clearly identified at about 20% sulfonation level. We have found that changing the model of S-SIBS polymer architecture from a random distribution of sulfonated groups to a “blocked distribution” can increase diffusion of water leading to a percolation threshold at lower sulfur content. Finally, the mean-field dynamic density functional theory was utilized to obtain the morphology for a range of triblock and three-arm star SIBS block copolymers at the mesoscale level. Using these results the permeability of water was calculated via the finite element method. We have confirmed that SIBS forms a hexagonal morphology that is transformed to lamellar upon sulfonation and water uptake. We have found a variety of morphologies for small slabs of SIBS that depend on the strength of the surface field which we assume can be related to the solubility parameter of the solvent used to cast the polymer membranes.

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