

Multiscale Modeling Studies of Sulfonated Triblock Copolymers

Reporting in the journal *Molecular Simulation*,¹ researchers at Dynamics Science Inc., the Weapons and Materials Research Directorate, and Accelrys, Inc., have used a multiscale modeling approach to optimize the structure of sulfonated triblock copolymers.

Microphase separated copolymers are of considerable industrial interest as different phases show different properties, such as one phase (elastomeric) being impermeable to water but lightweight and flexible whilst another phase (ionic) being highly water permeable – ideal for protective yet breathable textiles.

Sulfonated polystyrene-polyisobutylene-polystyrene (SIBS) triblock copolymers were studied owing to their promising applications for breathable yet protective textiles. They could also find use in fuel cell membranes. A multiscale modeling approach probed the static and dynamic properties for these polymer systems at detailed atomistic levels. The quantum density functional theory code DMol³ was used to understand the bonding of water molecules and sulfonate groups. Molecular dynamics tools (Discover with COMPASS parameters) were used to calculate the polymer density at various polymer sulfonation levels. Amorphous Cell was used to construct polymer bulk phases.

Polymer structures with both hydronium ions and water were studied, revealing a water self-diffusion mechanism where the hydronium ions move further away from the sulfonate groups with an increase in water content. Simulated water self-diffusion coefficients agreed well with experimental results.

Two different distributions of sulfonate groups were studied - one blocky and another perfectly dispersed. In the case of the blocky architecture, the water clusters are connected at a lower sulfonation level, leading to increased water diffusion coefficients compared to the dispersed architecture, indicating that polymers synthesized with the sulfonated groups blocked within the polystyrene base are desirable.

Mesoscale modeling, using the MesoDyn module, was used to study the effect of sulfonation on the phase morphology. The increase in sulfonation causes an increase in water concentration. The results from this show a change from a cylindrical phase to a lamellar phase upon sulfonation. Interestingly, the morphology was predicted to remain hexagonal if the triblock copolymer is sulfonated nonsymmetrically.

This study demonstrates both the usefulness and industrial relevance of a multiscale modeling approach.

“The multiscale simulations allowed us to study microphase separated polymeric systems, important for protective textiles or fuel cells leading to understanding of the underlying processes at the detailed atomistic level, not accessible by experiment, and to predict macroscopic properties at the mesoscale level that can be verified by experimental measurements,” said Jan Andzelm, Ph.D, Computational Chemist, U.S. Army Research Laboratory.

Reference

1. J. Andzelm, J. Sloan, E. Napadensky, S. McKnight, and D. Rigby, *Molecular Simulation*, **2006**, 32, 163–172.

Modules used

Materials Studio:

- Amorphous Cell
- COMPASS
- Discover
- DMol³
- MesoDyn

Industry sectors

Textiles - Protective Clothing
Fuel Cells

Organizations

Dynamics Science Inc., Aberdeen, MA

Weapons and Materials Research
Directorate, Aberdeen, MA

Accelrys, Inc

