Dynamic, Transport, and Mechanical Properties of Polymer Nanocomposites and Nanocomposite Solid Polymer Electrolytes

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ABSTRACT

Molecular dynamics simulations have been performed on PEO-based polymer nanocomposites and nanocomposite polymer electrolytes. MD simulations revealed that the PEO density is significantly perturbed by TiO_2 surfaces, PEO and ion dynamics in the vicinity of nanoparticles was found to be intimately related to the structure of the solid nanoparticle surfaces, polymer-surface interactions and the nanoparticle surface area in contact with the polymer.

Molecular dynamics simulations were coupled with the material point method calculations in order to allow prediction of mechanical properties of nanocomposites at length and time scales orders of magnitude larger than those accessible by molecular dynamics simulations.

Keywords: nanocomposites, molecular dynamics simulations, material point method

1 INTRODUCTION

Viscoelastic properties of polymer nanocomposites cannot be adequately described by conventional composite theories that do not take into account the size of particles and particle polymer interactions [1-2], indicating a need for fundamental understanding of the effect of nanoparticles on the structure and dynamics of the interfacial polymer. Molecular dynamics (MD) simulations are well suited for the investigation of structural and dynamic properties on the nanometer length scale. Coarse-grained MD simulations have provided valuable insight into factors responsible for alteration of polymer matrix properties with addition of interfaces; in particular, they found that the strength of nanoparticle – polymer interaction and nanoparticle specific surface area were the most important factors controlling properties of the interfacial polymer[1]. Addition of nanoparticles with attractive interactions led to the decreased polymer dynamics and increased viscosity, whereas addition of nanoparticles with the repulsive, or excluded volume, interactions led to increased polymer dynamics and decreased viscosity. These effects were found to scale linearly with the specific surface area of nanoparticles and not with the volume fraction was found for conventional composites. Another important factor controlling interfacial polymer dynamics is the structure of the surface, where interfacial polymer motion is strongly correlated to the surface structure [3].

Application of MD simulations to nanocomposites is limited to systems with a few nanoparticles because of high computational cost. To extend the length scale from the nanoscale to mesoscale and thus enable prediction of dynamic-mechanical properties of polymer nanocomposites with tens and hundreds of nanoparticles, we have coupled atomistic MD simulations with the material point method (MPM). This method is an extension of the particle-in-cell method that uses two representations of the continuum, one based on material points and the other based on a computational grid.

In this contribution we discuss influence of TiO_2 nanoparticles on poly(ethylene oxide) (PEO) and $PEO/LiBF_4$ dynamics and structure and show the path for coupling MD simulations with MPM calculations in order to obtain homogenized mechanical properties of polymer nanocomposites and nanocomposite polymer electrolytes.

We focus on the PEO/TiO_2 system because PEO is a major component of the PEO-based solid polymer electrolytes, such as $PEO/LiBF_4/TiO_2$, which are potential candidates for use in the solvent-free secondary lithium batteries. Addition of ceramic nanoparticles to polymer electrolytes, initially done to enhance mechanical properties, has been also found to improve anodic stability, cyclability, sometimes conductivity and cation transfer number of polymer electrolytes without causing any observed degradations.

2 PEO-T$_i$O$_2$ INTERACTIONS

MD simulation studies of the interface between poly(ethylene oxide) (PEO) and TiO_2 have been performed at 423 K using a quantum chemistry based force field. MD simulations revealed that the PEO density is significantly perturbed by TiO_2 surfaces, forming layers of highly dense polymer (compared to the bulk melt) that persisted up to 15 Å from the surface. Conformational and structural relaxations of the interfacial PEO were found to be dramatically slower than those of bulk PEO as shown in Figure 1. These effects are attributed to intrinsic slowing down of PEO dynamics and increased dynamic heterogeneity of the interfacial polymer. The surface structure and electrostatic interactions between PEO and TiO_2, rather than the increased polymer density at the TiO_2

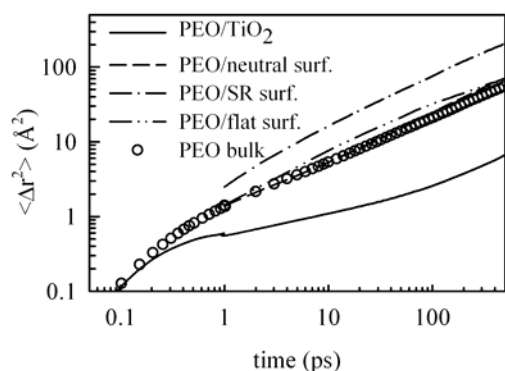surface, determine the nature of PEO relaxation at the TiO$_2$ interface.

Figure 1. Mean-square displacements for the interfacial PEO backbone atoms next to TiO$_2$, flat, neutral, soft-repulsive surfaces and bulk PEO.

MD simulations of PEO between flat (structureless) surfaces with interactions modified to match PEO density profiles to those of the PEO between the atomistic TiO$_2$ surfaces revealed no significant differences between the structural and conformation relaxation of the interfacial PEO and the PEO bulk (see Figure 1), indicating that the PEO density near surfaces has only a minor influence on interfacial PEO dynamics and that perturbation of the interfacial PEO dynamics near TiO$_2$ surfaces is largely due to atomistic structure of the TiO$_2$ surfaces and not densification of interfacial PEO.

Elimination of the Coulomb interactions between PEO and TiO$_2$ significantly increased the structural and conformational relaxation of the interfacial PEO, demonstrating that these interactions are responsible for the slow down of PEO dynamics. Moreover, relaxation of the interfacial PEO in the PEO/neutral surface system is similar to that in bulk PEO suggesting that the surface with the TiO$_2$ structure and no Coulomb interaction with PEO do not significantly perturb PEO dynamics. Reduction of the repulsive interaction between the neutral surface and PEO further facilitated relaxation of the interfacial PEO in agreement with the results polymer films simulations in vacuum.

We conclude that in addition to such intrinsic parameters as torsional potentials, the polymer-surface interactions and surface structure (at least for attractive polymer surface interactions) are two fundamental factors that determine interfacial polymer relaxations in PEO/TiO$_2$ nanocomposites.

3 PEO/LiBF$_4$/TiO$_2$ NANOCOMPOSITES

Addition of a TiO$_2$ nanoparticle to PEO/LiBF$_4$ solid polymer electrolyte resulted in formation of the highly structured layer with the thickness of 5-6 Å as seen from Figure 2 that has more than an order of magnitude slower mobility than that of bulk PEO/LiBF$_4$. The PEO and ions in the layers extending from 6Å to 15 Å from the TiO$_2$ nanoparticle also revealed some structuring and reduced dynamics, whereas the PEO/LiBF$_4$ located further than 15 Å was basically unaffected the presence of the TiO$_2$ nanoparticle. Both cation and anion tended to form a region with the increased concentration in the interfacial layers extending from 5 Å to 15 Å. No ions were dissolved by the first interfacial layer of PEO. Addition of the nanoparticle with the soft-repulsion interactions with PEO resulted in formation of the PEO interfacial layer with reduced PEO density but increased ion concentration. The PEO and ion mobility in the interfacial layer next to the soft-repulsive nanoparticle were higher than those of bulk PEO/LiBF$_4$ by 20-50%, whereas conductivity of nanocomposite electrolyte with the soft-repulsive particle increased only by 10%.
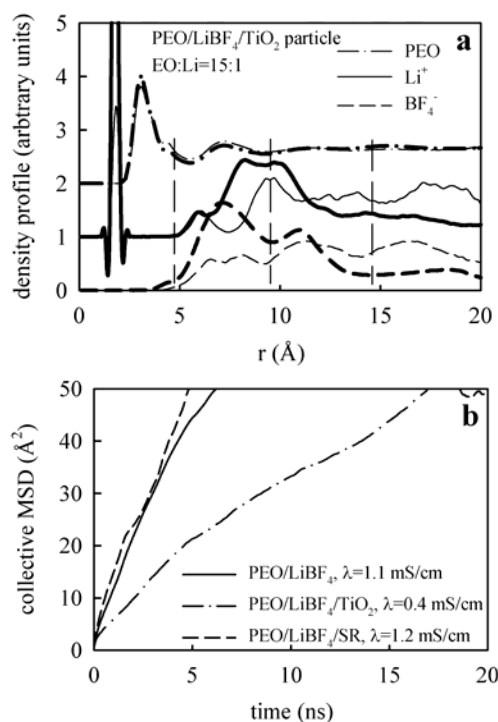

Figure 2. Density profiles for PEO/LiBF$_4$/TiO$_2$ and collective mean-square displacements for PEO/LiBF$_4$ with TiO$_2$ and soft-repulsive particles embedded in polymer electrolytes

4 COUPLING OF MD SIMULATIONS AND MPM CALCULATIONS

In the previous sections, we have shown that the nature of the polymer-nanoparticle interactions and the structure of the nanoparticle surface significantly perturb structural, transport and dynamic properties of polymers and polymer electrolytes. In this section we will demonstrate that mechanical properties extracted from MD simulations can be used in MPM calculation in order to obtain homogenized properties of nanocomposites at much larger length-scales.

MD simulations have been performed on three systems: (a) pure polymer and (b) polymer nanocomposite consisting of an elastic cylinder embedded in a polymer matrix with the polymer having the same interactions with the cylinder as with itself (neutral system), (c) polymer nanocomposite consisting of an elastic cylinder embedded in a polymer matrix with the polymer interacting with the cylinder twice as strong as with itself (attractive system). The system is shown in Figure 3.
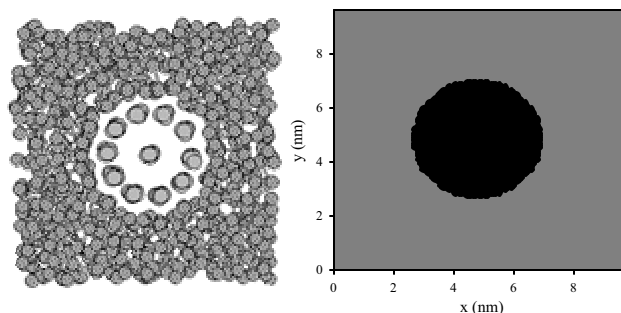

Figure 3. Snapshot of the MD simulation system consisting from a cylinder in a polymer Rcyl=2.1 nm, box size=9.615 nm (left) and setup of the MPM run (right).

Shear modulus G(t) has been extracted from MD simulations and approximated with a sum of 3 exponents. Bulk modulus (K) of the polymer was assumed to be time independent. Elastic properties of the cylinder were also measured in MD simulations. The properties ($K_{polymer}$, $G(t)polymer$ and K_{cyl}, G_{cyl}) extracted from MD simulations were used in MPM simulations of the composite.

A number of stress relaxation, creep, and dynamic-mechanical experiments have been performed on the pure materials and composites. Stress relaxation experiments are the most efficient and allow property extraction and are accurate to within 1 % for pure polymer MPM calculations. Stress on the material points have been found to exhibit large oscillations during MPM calculations. However, averaging over material points reduced oscillations for the composite and virtually eliminated them for the pure viscoelastic material. The velocity damping function had to be added to the particle equation of motions to significantly reduce the oscillations, while leaving the average (smoothed) G(t) behavior of the composite unchanged. A series of computational experiments indicated that the shear

modulus for the composite not only increases in magnitude and shows significantly longer relaxation times, but the shape of the relaxation becomes more stretched.

MPM calculation of the neutral system using properties of the pure polymer and elastic material from MD simulations predicted shear modulus of the composite in good agreement with the one obtained from MD simulations without any adjustment to the polymer or nanoparticle properties. In order to reproduce in MPM calculations the shear modulus G(t) from MD simulations of the nanocomposite with the attractive polymer-nanoparticle interactions, we introduced a layer of polymer around a nanoparticle that has relaxation two orders of magnitude slower than the bulk polymer and the width of 1.7 nm corresponding to approximately 1.7 layers of polymer. This model was able to reproduce MD simulations results reasonably well as shown in Figure 4. We are currently working on extending this model to systems with more than one nanoparticle and investigating the ability of this model to capture the dependence of shear modulus for attractive nanocomposites on the size of nanoparticles.
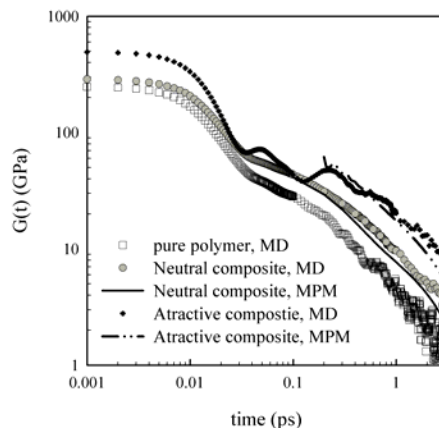

Figure 4. Shear modulus of bulk polymer, neutral and attractive nanocomposites from MD simulations and MPM calculations.

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