

## Special Feature: Organic Materials

Research Report

### Atomistic and Mesoscopic Simulations for Polymer Materials

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**■ABSTRACT■** Recent applications of atomistic and mesoscopic simulations for polymer materials are presented. Molecular dynamics simulations have been performed to investigate the CO<sub>2</sub> induced plasticization of a polyetherimide (PEI). With increasing temperature, CO<sub>2</sub> molecules become to diffuse by continuous motion throughout PEI from the jumping motion among the preferential sites under the glass transition temperature. This enhances the motion of PEI atoms, and results in the plasticization of PEI. The crossing dynamics at an entanglement point of surfactant threadlike micelles was studied using a mesoscopic simulation method, the dissipative particle dynamics (DPD). We concluded that the breakage of the threadlike micelles is an essential process in the relaxation mechanism, and a phantom crossing can be seen as a special case. We also studied the mesoscopic structure of the perfluorinated sulfonic acid membrane Nafion containing water using the DPD simulation. Water particles and hydrophilic particles of Nafion side chains spontaneously form aggregates and are embedded in the hydrophobic phase of the Nafion backbone. The cluster size and its dependence on the water content are in good agreement with experimental reports. A novel method to simulate evaporation process of polymer solution was proposed using the DPD. Evaporation model and effective mass are introduced to the conventional DPD method, and this method successfully demonstrated the phenomenon.

**■KEYWORDS■** Computer Simulation, Dissipative Particle Dynamics, Threadlike Micelle, Phantom Crossing, Polyelectrolyte Membrane, Mesoscopic Structure, Morphology, Drying Process

#### 1. Introduction

Atomistic and mesoscopic simulations are widely used to investigate structural and rheological properties of polymer materials. The former is based on the dynamics of atoms using a forcefield. It is faithful to molecular structure and property, however, has a limitation for size and time scales to be handled in the computer. On the other hand, in a mesoscopic method some structures are eliminated by a coarse-grained procedure. Although some information is omitted in this method, much larger size and longer time scales can be analyzed. Each of these two methods has merits and demerits, therefore we should choose a method for the problem and interest. Some applications in our recent studies are presented for these two methods.

#### 2. Atomistic Simulation

Atomistic simulations such as molecular mechanics (MM) and molecular dynamics (MD) are applied to analyze the structure of crystal/amorphous and the

interaction at surface/interface of polymer materials in order to understand the phenomena in an atomistic level. Recently, we performed MD simulations to investigate the CO<sub>2</sub> induced plasticization of a polyetherimide (PEI).<sup>(1)</sup> Atomistic packing models of PEI are created for several CO<sub>2</sub> contents up to 12 wt%, by inserting CO<sub>2</sub> molecules into the free volume of PEI (Fig. 1). MD simulations are carried out using the

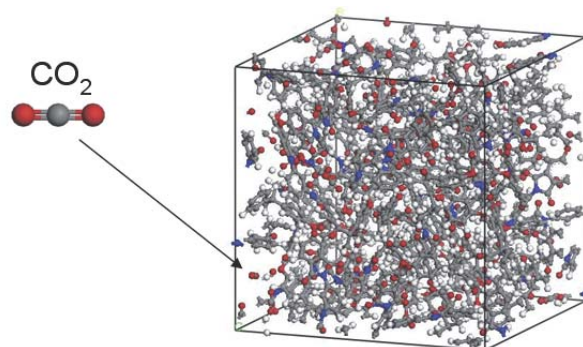


Fig. 1 Atomistic packing model of PEI with 12 wt% CO<sub>2</sub>.

Forcite module in Materials Studio (Accelrys) with the COMPASS forcefield and the group based summation method. The temperature and pressure are controlled by the Nose and Andersen methods, respectively. The glass transition temperature (Tg) is estimated based on the relation between specific volume and temperature.

The depression of Tg is observed as increasing the CO<sub>2</sub> content, and it is quantitatively consistent with the experimental results of the dynamic viscoelasticity. The radial distribution functions between CO<sub>2</sub> and PEI atoms reveal that CO<sub>2</sub> preferentially exist in the imide and ether sites under Tg. CO<sub>2</sub> molecules diffuse by the jumping motion among the preferential sites at 200K and 400K as shown in Fig. 2. With increasing temperature (600K), CO<sub>2</sub> molecules become to diffuse by continuous motion throughout PEI and enhance the motion of PEI atoms, and results in the plasticization of PEI.

### 3. Mesoscopic Simulation

For a mesoscopic scale, some simulation methods such as mean-field (MF) and dissipative particle dynamics (DPD) are proposed to understand phenomena in mainly qualitative aspects. Here, three applications of DPD shall be introduced. Before showing the applications, the procedure of DPD is presented.

#### 3.1 DPD Simulation Method

The DPD is a relatively new method proposed to study hydrodynamic behavior of complex fluids. The method is based on the dynamics of soft particles interacting by conservative, dissipative, and random forces. By introducing a bead-spring type particle

model, the method is extended to polymer systems. Here we describe an outline of the model and the evolution algorithm of the DPD. Now, we consider that the particles are subject to conservative, dissipative, and random forces, and spring forces for connecting spheres. The time evolution of the system is obtained by solving Newton's equation of motion,

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i \dots \dots \dots (1)$$

$$m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i \dots \dots \dots (2)$$

where  $\mathbf{r}_i$ ,  $\mathbf{v}_i$ , and  $m_i$  are the position, velocity, and mass of the  $i$ -th particle, respectively. The force  $\mathbf{f}_i$  contains three parts of the original DPD formula and an additional spring force for the polymer system. The interaction between two particles can be written as the sum of these forces, where the suffixes  $C$ ,  $D$ ,  $R$ , and  $S$  represent the conservative, dissipative, random, and spring forces, respectively.

$$\mathbf{f}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R + \mathbf{F}_{ij}^S) \dots \dots \dots (3)$$

The first three forces of the original DPD are considered within a certain cutoff radius  $r_c$ . The conservative force  $\mathbf{F}_{ij}^C$  is a soft repulsion acting along the line of centers and is given by

$$\mathbf{F}_{ij}^C = \begin{cases} -a_{ij}(r_c - r_{ij})\mathbf{n}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases} \dots \dots \dots (4)$$

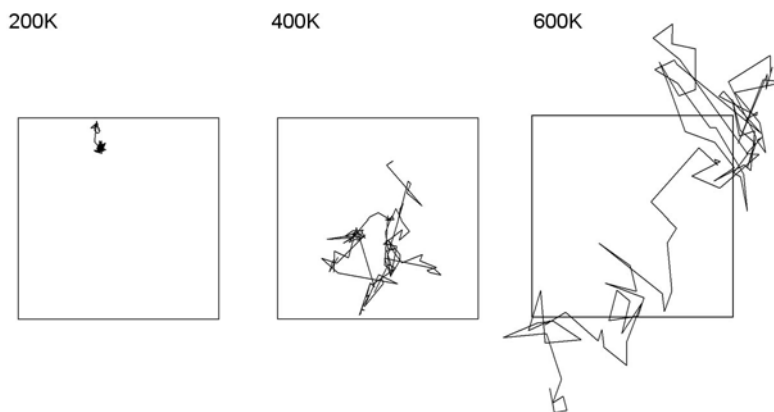


Fig. 2 Trajectories of a representative CO<sub>2</sub> molecule during 1ns dynamics at 200K, 400K, and 600K.

where  $a_{ij}$  is a maximum repulsion force between particle  $i$  and  $j$ ,  $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ ,  $r_{ij} = |\mathbf{r}_{ij}|$ , and  $\mathbf{n}_{ij} = \mathbf{r}_{ij} / |\mathbf{r}_{ij}|$ . The repulsion parameter between water particles ( $a_{ii}$ ) is set at  $25k_B T$  for density  $\rho = 3$  to match the compressibility of liquid water at room temperature, if one DPD particle corresponds to one water molecule. The dissipative force  $\mathbf{F}_{ij}^D$  is a hydrodynamic drag and is given by

$$\mathbf{F}_{ij}^D = \begin{cases} -\gamma \omega^D(r_{ij}) (\mathbf{n}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{n}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases} \dots \dots \dots (5)$$

where  $\gamma$  is a friction parameter,  $\omega^D(r_{ij})$  is the weighting function, and  $\mathbf{v}_{ij} = \mathbf{v}_j - \mathbf{v}_i$ . The friction parameter is related to the viscosity of the system and acts in such a manner as to slow the relative velocity of two particles and to remove kinetic energy. The random force  $\mathbf{F}_{ij}^R$  corresponds to thermal noise and is governed by the noise parameter  $\sigma$  and a different weighting function  $\omega^R(r_{ij})$  as follows.

$$\mathbf{F}_{ij}^R = \begin{cases} \sigma \omega^R(r_{ij}) \zeta_{ij} \Delta t^{-1/2} \mathbf{n}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases} \dots \dots \dots (6)$$

The randomness is contained in the element  $\zeta_{ij}$ , which is a randomly fluctuating variable with Gaussian statics.

$$\langle \zeta_{ij}(t) \rangle = 0 \dots \dots \dots (7)$$

$$\langle \zeta_{ij}(t) \zeta_{kl}(t') \rangle = (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta(t - t') \dots \dots \dots (8)$$

They are uncorrelated for different pairs of particles and time. There is a relation between the two weighting functions and two parameters.

$$\omega^D(r) = [\omega^R(r)]^2 \dots \dots \dots (9)$$

$$\sigma^2 = 2\gamma k_B T \dots \dots \dots (10)$$

In our simulation, we choose weighting functions as follows,

$$\omega^D(r_{ij}) = [\omega^R(r_{ij})]^2 = \begin{cases} (r_c - r_{ij})^2 & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases} \dots \dots \dots (11)$$

The appearance of  $\Delta t^{-1/2}$  in Eq. 6 is due to ensuring the consistent diffusion of particles independent of the stepsize of the integration as discussed by Groot and Warren.<sup>(2)</sup> The spring force  $\mathbf{F}_{ij}^S$  for a polymer is considered to be harmonic springs for the equilibrium bond distance  $r_s$ ,

$$\mathbf{F}_{ij}^S = -C(r_s - r_{ij}) \mathbf{n}_{ij} \dots \dots \dots (12)$$

where  $C$  is a spring constant.

In our study, we choose the interaction range  $r_c$ , the temperature  $kT$  and the particle mass  $m$  as the units of length, energy and mass, respectively. The noise parameter  $\sigma$  is set at 3.0 (the friction parameter  $\gamma$  is 4.5). We set the bond distance at  $r_s = 0.86$  for the average distance of the nearest neighbor at a particle density  $\rho = 3$  and the spring constant at  $C = 100$ . Time evolution of the system is calculated by a modified version of the velocity-Verlet algorithm at  $\lambda = 0.65$  with time steps of  $\Delta t = 0.05$ . Our original DPD program has been coded and is used for following simulations.

### 3.2 Crossing Dynamics of Threadlike Micelles

Surfactants spontaneously aggregate to form a wide variety of assemblies in an aqueous solution, such as spherical and rodlike micelles, bilayer membranes, and vesicles. In particular, surfactant threadlike micellar solutions exhibit pronounced viscoelastic behavior as well as polymer systems with an entanglement. Some surfactants, such as cetyltrimethylammonium bromide containing sodium salicylate, form long and stable threadlike micelles in an aqueous solution. In such threadlike micellar solutions, the relaxation mechanism is completely different from that of a concentrated polymer system having broad relaxation spectra. The threadlike micellar system shows a Maxwell type relaxation with a single relaxation time. This difference between a threadlike micellar system and a polymer system is explained on the basis of structural features of the threadlike micelles and polymer chains. The latter is constructed by the

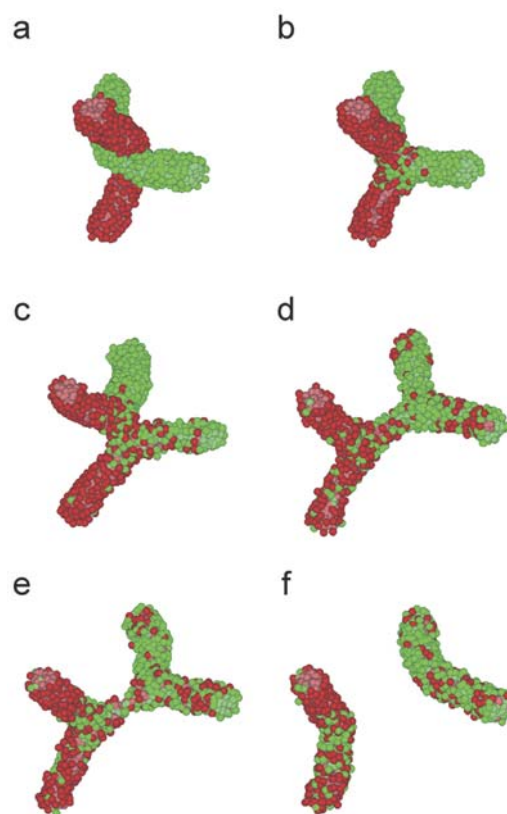
formation of covalent bonds between constituent atoms of the polymer chains, which are usually not easily broken. Meanwhile, the former is constructed via intermolecular interactions of surfactants. Therefore, threadlike micelles can recombine their structure, which involves breakdown and reformation. In regard to this point, the relaxation mechanism of the threadlike micellar system has been discussed, with focus on a kind of reactivity of the micelles, or recombination of the structure. Shikata et al. proposed *the phantom network model* to explain the relaxation behavior at an entanglement point of the threadlike micelles.<sup>(3)</sup> In their model, the threadlike micelles fuse at an entanglement point to form a four-armed branch point, which is followed by passage through each other like a phantom. According to their experimental observations, it was reported that such crossing of threadlike micelles is a dominant process rather than breakdown anywhere along the micelles. They pointed out that terminals of threadlike micelles, which might be generated by breakdown of the micelles, are scarcely seen with electron micrograph observation, therefore a breakdown of threadlike micelles is less likely to occur. Although the viscoelastic behavior of threadlike micellar solutions can be well explained using such crossing models, the actual dynamics at an entanglement point could not be directly observed. Therefore, there is a requirement to clarify how this process occurs.

The DPD simulation was applied to study the crossing dynamics at an entanglement point of surfactant threadlike micelles in an aqueous solution.<sup>(4)</sup> The surfactant molecule is represented by a coarse-grained model, which contains hydrophilic head and hydrophobic tail groups. Water is also modeled by the same size particles as those adopted in the surfactant model, corresponding to a group of several water molecules. It is confirmed that the threadlike micelle is stabilized with a moderate repulsive force between hydrophilic head groups. When two threadlike micelles are encountered at an entanglement point, they fuse to form a four-armed branch point. Then, a phantom crossing is occasionally observed after elongation of the branch point (**Fig. 3**). A cutting down of one of the threadlike micelles at the branch point was also frequently observed. If the repulsive force between head groups is strengthened, one of the micelles becomes easily broken down at an entanglement point before fusion. In these three schemes (phantom crossing, cut down, and break

down) shown in **Fig. 4**, the breakage occurs at somewhere along the threadlike micelle. This breakage may be an essential process in the relaxation mechanism, and a phantom crossing can be seen as a special case of these processes. A possible mechanism was also presented; a terminal vanishing model, in which the generated terminal merges into the connected micelle part due to thermal motions.

### 3.3 Mesoscopic Structure of Polyelectrolyte Membrane

The well-known perfluorinated sulfonic acid membranes Nafion are the most common membrane materials used in the polymer electrolyte fuel cell because of their exceptional chemical, thermal and mechanical stability in addition to their reasonable proton conductivity. A Nafion polymer consists of a polytetrafluoroethylene backbone and perfluorinated

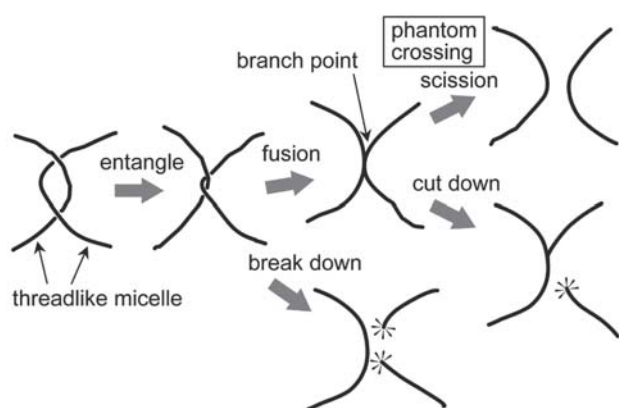


**Fig. 3** Snapshots of time evolution for a phantom crossing process. The images are taken at simulation times of (a) 340, (b) 370, (c) 500, (d) 650, (e) 670, and (f) 700. Two threadlike micelles fuse to form a branch point, and then two individual micelles are reproduced by the scission after an elongation of the branch point.



pendant side chains terminated by sulfonic acid groups. To investigate the structure and swelling behavior of the hydrated Nafion membranes, numerous experimental efforts have been concentrated on neutron, wide and small angle X-ray scattering, IR and Raman spectroscopy, and TEM techniques. It has been well established that hydrated Nafion membranes have two phases on a nanometer scale, a hydrophobic phase containing the backbone and a hydrophilic phase containing sulfonic acid groups with water. Several models for these structures such as the interconnected spherical water clusters have been proposed for the interpretation of the scattering patterns. However, these models are still under discussion concerning the size and shape of the water clusters. It is meaningful to clarify the structure of the membranes for analytical study and to improve the mechanical and transport properties of the materials.

We have applied the DPD simulation to study the structure of hydrated Nafion membranes.<sup>(5,6)</sup> Nafion polymer molecules are constructed by connecting soft DPD particles based on molecular structure. A water particle is also modeled as the same size particle as the Nafion polymer model. This means that the water particle represents a group of several H<sub>2</sub>O molecules. The repulsion parameter between DPD particles is related to the Flory-Huggins interaction parameter. They are estimated by an atomistic simulation calculating the mixing energies for pure components of DPD particles and their mixtures. The mixtures of Nafion polymer particles and water particles spontaneously form a sponge-like or porous structure

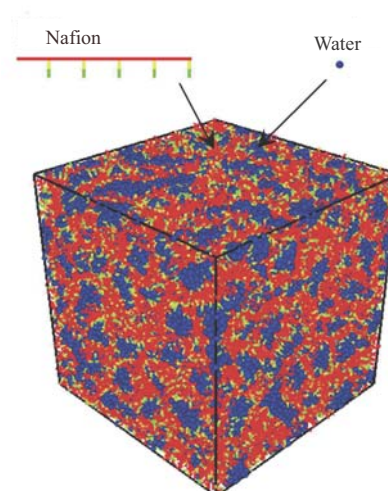


**Fig. 4** Schematic illustration of the crossing dynamics at an entanglement point of surfactant threadlike micelles, summarized according to the simulation results.

(**Fig. 5**). Water particles and hydrophilic particles of the Nafion side chain form aggregates or clusters and are embedded in the hydrophobic phase of the Nafion backbone. The bicontinuous structure of the Nafion backbone and water is recognized. It is an essentially identical but more realistic structure than some proposed models based on experimental studies. The size and spacing of water clusters are determined by calculating the radial distribution of water particles for equilibrium structures of the hydrated Nafion membranes for 10-30 vol% water content. The cluster size of the simulation model changes by 3.2 to 5.0 nm and its spacing changes by 3.6 to 6.0 nm. These magnitudes of water clusters and their dependence on the water content are in agreement with experimental reports.<sup>(7)</sup> The simulated mesoscopic structure is confirmed to be highly possible for hydrated Nafion membranes.

### 3.4 Drying Process of Polymer Films

The drying process of polymer solutions plays an important role in formation of polymer films and coatings. To understand and optimize solvent diffusion, which is a dominant process of this phenomenon, various diffusion models based on the free-volume concept have been proposed.<sup>(8)</sup> The prediction results are mostly comparable with experimental data and can be utilized for design and optimization of processing operations. In some cases, however, inhomogeneous



**Fig. 5** Simulated morphology of the 20 vol% hydrated Nafion membrane system. Nafion polymer particles are indicated by lines and water particles are drawn by spheres.

aspects such as migration of solvent molecules and phase separation of polymers become important. Such microscopic phenomena are beyond previous diffusion models<sup>8)</sup>, therefore novel methodology is required. Though molecular dynamics (MD) stands at such a microscopic concept, MD is limited to a relatively small number of molecules due to computational costs. Considering the scale of phenomenon where a typical thickness of polymer films is over  $\mu\text{m}$  order, coarse-grained model seems to be appropriate for this problem rather than conventional molecular dynamics technique.

A method to simulate evaporation process of polymer film was proposed using the DPD.<sup>(9)</sup> Evaporation model and effective mass ( $m$ ) are introduced to the conventional DPD method. In the evaporation model, when solvent particle comes into gas phase above the polymer solution, it is replaced to gas particle judging as evaporated. Effective mass plays to restrain mobility of polymer particle and to decrease solvent diffusivity at low concentration. In **Fig. 6**, snapshots of the drying process of polymer solutions are depicted for two cases; (a)  $m = 100$  and

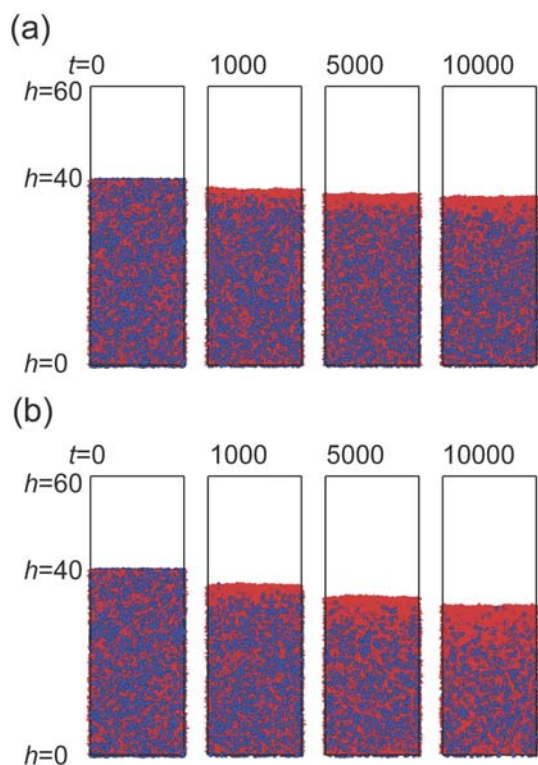
(b)  $m = 6.25$ . Polymer and solvent particles are drawn by spheres, however, gas particles are not shown in the figure. It is recognized that solvent particles evaporate from the surface of the polymer solution and thickness of polymer films become thinner. In the case of (a), drop of diffusivity at low concentration is much remarkable, the surface of polymer film dries up and skin region is formed. On the other hand, in the case of (b), dry up region is moderate and solvent gradually evaporate throughout film. With the help of additional techniques an evaporation phenomenon is simulated in successful.

#### 4. Conclusions

Recent applications of computer simulation were presented in this paper. The computer simulation is helpful to understand phenomena, however, it is not almighty. We should use it with the knowledge of assumption and limitation of the method.

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**Fig. 6** Snapshots of drying behavior at several simulation times; (a)  $m=100$  and (b)  $m=6.25$ . Gas particles are not indicated.

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Figs. 3 and 4

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Fig. 6

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