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出版情報：COE Lecture Note. 39, pp.46-54, 2012-03-13. 九州大学マス・フォア・インダストリ研究所
バージョン：
権利関係：

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Abstract

In this article, we introduce recent activities of multiscale polymer modeling aimed for material design in industry. To design the polymer material with expected properties, we need to predict polymer structure, and study the relation between the structure and properties. However, polymer structure is hierarchical, and has a wide range of length scale and time scale. Thus, multiscale and hierarchical modeling are necessary to apply computational simulation to polymer material design. OCTA had been developed for such a hierarchical polymer modeling. OCTA includes several simulation programs, which are based on different physical model, and focus on different length scale and time scale. Some studies of hierarchical modeling of polymer have been conducted using OCTA. We describe an overview of OCTA, and an example of the study of the structure and mechanical properties of the interface of polymer blends.

1. Introduction

Polymer materials such as plastics, rubber, film and fiber are widely used for industrial products. Not only conventional bulk materials, polymer materials are also used in many high-tech materials such as electric devices, battery and artificial organ. Various kinds of function are required for such polymer products. For example, mechanical properties such as modulus and strength are important for construction materials, and electrical and optical properties such as dielectric constant and reflective index are important for electric devices and optical films. Since such functions and properties are controlled by the structure of polymers, main objective of polymer material design is to design the structure of polymers and to predict the properties of the materials from the structure.

However, the structure of polymers includes very wide range of length scale and time scale. Figure 1 shows examples of various polymer structures. Chemical structure of monomer unit is a finest structure of polymers. The topological structure of polymer chain is not simple. Not only linear chains, some polymer molecules have branched structure, and the length of chains corresponding molecular weight is not the same, and has a distribution even in same polymer products such as polyethylene, polystyrene and so on. In addition to the molecular structure, crystalline structure and phase separated

structure are examples of higher order structure. Furthermore, crystal structure itself has a hierarchical structure, i.e. atomic coordinate in crystalline lattice is the finest crystal structure, and lamella, shish kebab and spherulite structure are higher order crystal structure. Since the polymer structure includes such a wide range of scale, multi scale and multi physics modeling is necessary to design polymer materials.

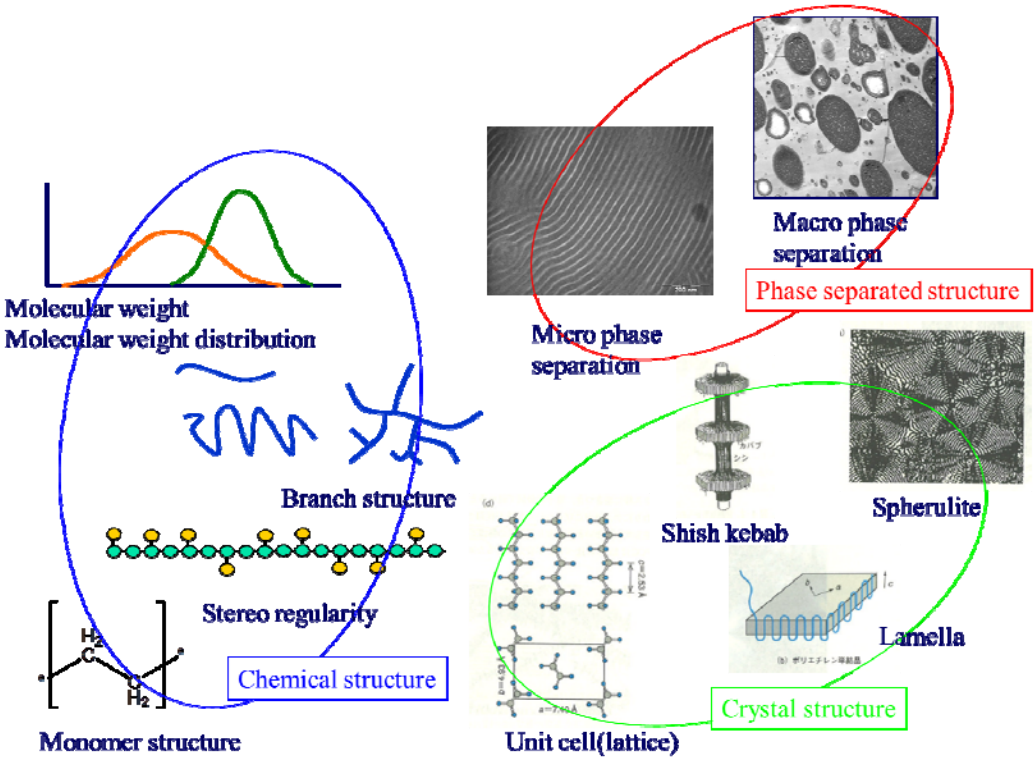

Figure 1 Example of polymer structure

Furthermore, various simulation methods are necessary to study such a hierarchical structure and many kinds of functions and properties of polymer materials. For examples, quantum physics and chemistry are needed to study electrical and optical properties. Molecular dynamics simulation will be applied to study bulk structure of polymer. However, since polymer chain has a large molecular weight and long time scale of dynamics, it is hard to apply conventional molecular dynamics simulation to realistic polymer system even though using powerful computational hardware. Thus coarse-grained models are also needed to study higher order polymer structures.

OCTA (Open Computational Tool for Advanced material technology) [1] is a simulation platform aimed for covering such a wide range of polymer structure. The OCTA was developed in a national project of Japan, and then the OCTA was opened for

the public after the project finished. From the release of the first version of OCTA in April 2002, it has been maintained by many collaborators, and the researchers in more than 1000 sites have become the users.

We will introduce the overview of OCTA in the following section and an example of hierarchical modeling to study of structure and mechanical properties of the interface of polymer blends.

2. Overview of OCTA

The concept of OCTA is shown in Figure 2. The OCTA contains several simulation programs (engine) and user interface (platform). Each engine is based on different physical models, and covers different length scale and time scale. Furthermore, collaborative operations between engines are conducted to obtain realistic structures and properties of soft materials.

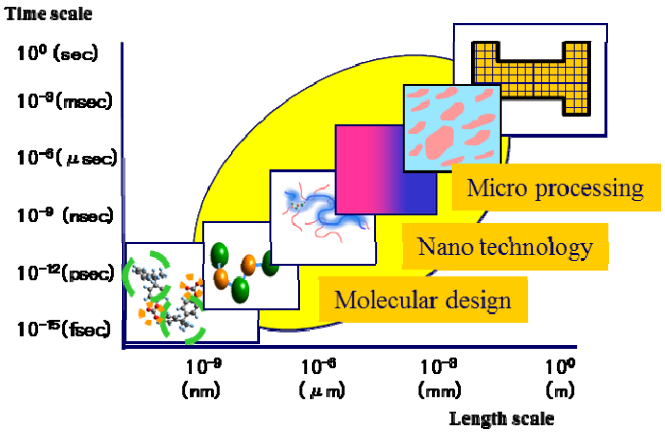

Figure 2. The concept of OCTA

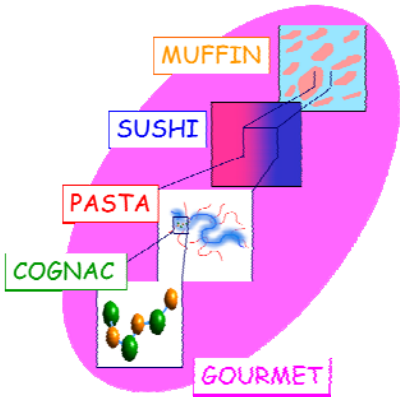

Figure 3. Computational programs in OCTA

Figure 3 shows computational programs in OCTA. OCTA originally contains four engines, COGNAC, PASTA, SUSHI and MUFFIN, and a graphical user interface, GOURMET. The overview of each engine is shown in the following.

2.1. COGNAC (COarse Grained molecular dynamics program by NAgoya Cooperation)[2]

COGNAC is a general purpose coarse-grained molecular dynamics (MD) program, which focus on the structure and dynamics of polymer chains. Using coarse-grained model, realistic length of polymer chains can be put into the simulation system, and some multiphase structures such as nano-composites and micro phase separated structure of block copolymers can be studied. Figure 4 shows example of multiphase

structures studied by COGNAC.

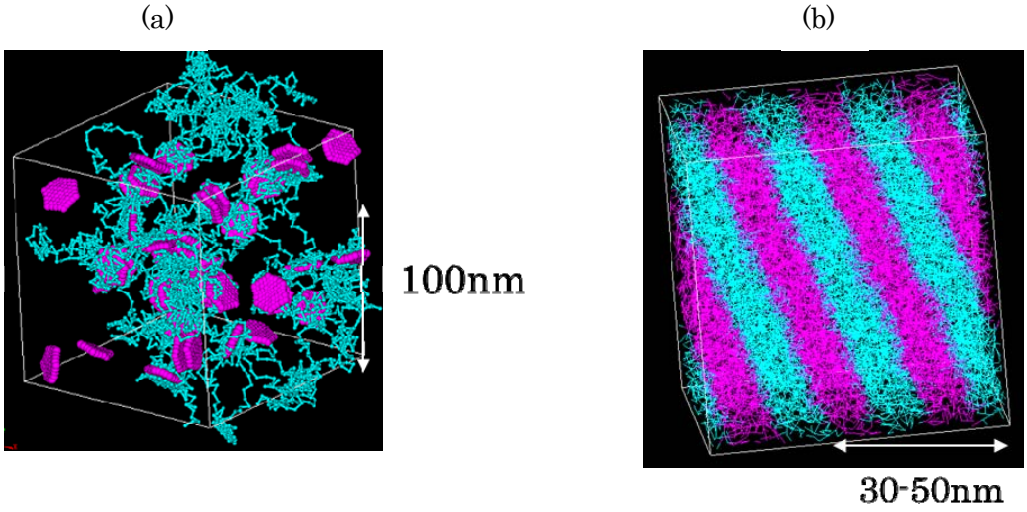

Figure 4. Examples of multiphase structures studied by COGNAC, (a) polymer-clay nano composite (b) micro phase separated structure of diblock copolymer. Scales in figures show typical values, and depend on the coarse-graining method.

2.2. PASTA (Polymer rheology Analyzer with Slip-link model of enTAnglement)[3]

PASTA is based on slip-link model, and predicts the viscoelastic properties of polymer melts. A unit of length scale of coarse-graining is entanglement length, which typically have molecular weight from 1,000 to 10,000. With this highly coarse-grained model, we can predict viscoelastic properties, such as storage modulus G', loss modules G" and steady state viscosity η, of realistic molecular weight and molecular weight distribution.

2.3. SUSHI (Simulation Utilities for Soft and Hard Interfaces)[4]

SUSHI is a tool for predicting self-assembly structures such as micro phase separation of block copolymers, interfacial structures of polymer blends and structures of micelles. SUSHI is based on mean field theory and topology of polymer chain is described by path integral. SUSHI output equilibrated fields of polymer segment density by iterative calculation of self-consistent filed (SCF). Dynamics of density field also can be obtained by solving diffusion equation. Figure 5 show examples of the output of SUSHI.

(a)

(b)

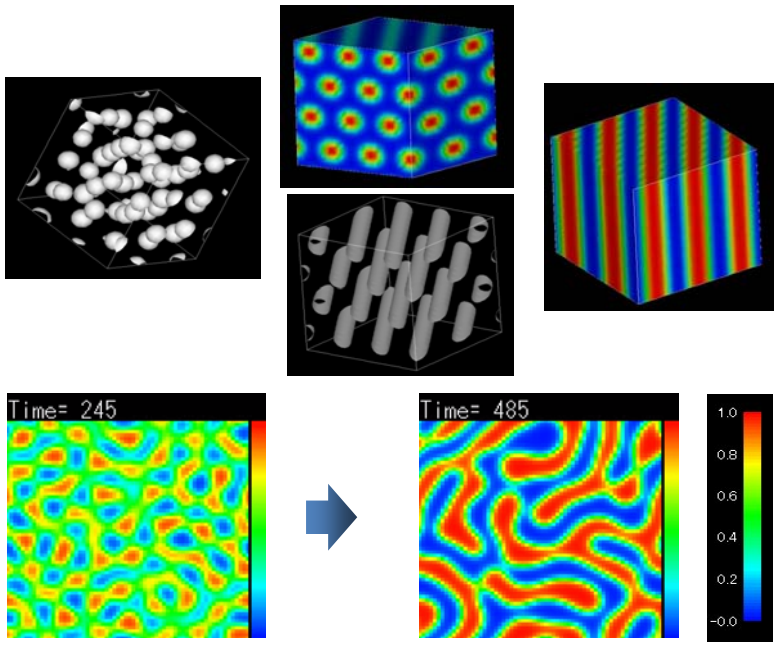

Figure 5 Examples of the output of SUSHI, (a) equilibrated morphology of diblock copolymers at various ratio of block length, (b) dynamics of the phase separation of polymer blend.

2.4. MUFFIN (MultiFarious FIeld simulator for Non-equilibrium system)

MUFFIN is a tool for multi-phase structure such as phase separation of polymer blends, suspensions and emulsions. MUFFIN has modules both for fluids and solids. Fluid modules of MUFFIN can handle phase separation of polymer blends, dynamic of droplet in fluids with taking fluid dynamics and electrostatic interaction into account. Solid modules calculate linear elastic behavior of complex multi-phase morphology using finite element method.

3. Example of hierarchical modeling[5,6]

An example of hierarchical modeling is shown in this section. Coarse-grained MD simulation and SCF calculation has been conducted to examine the structure and strength of a polymer interface reinforced with block copolymers. We studied the interface of A-homo/AB-diblock/B-homo polymer systems. Since the time scale of polymer chain dynamics is very long, it's difficult to obtain the equilibrated interfacial structure even by the coarse-grained simulation. Thus, we developed original algorithm, the density-biased Monte Carlo method[2], in which equilibrated morphologies are obtained by the SCF calculation, then the initial configurations of polymer chains for

coarse-grained MD are generated from the obtained density distribution of each segments. Figure 6 shows density profile of A100/B100 blend and A100/A50B50/B100 blend (numbers after bead type A and B correspond to a number of beads in a chain) obtained from the SCF calculation, and Figure 7 shows snapshot structures of coarse-grained MD which correspond to the results of SCF calculation.

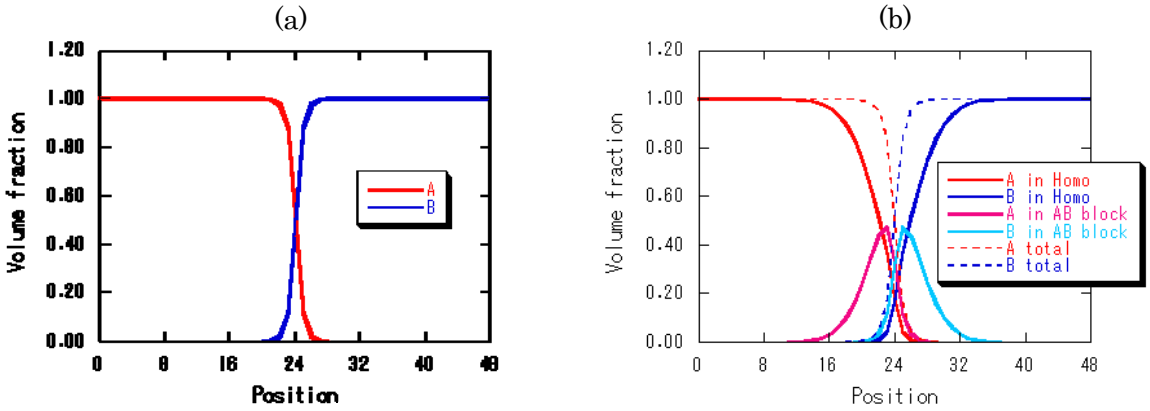

Figure 6 Density profile of each segment type, (a) A100/B100, (b) A100/A50B50/B100.

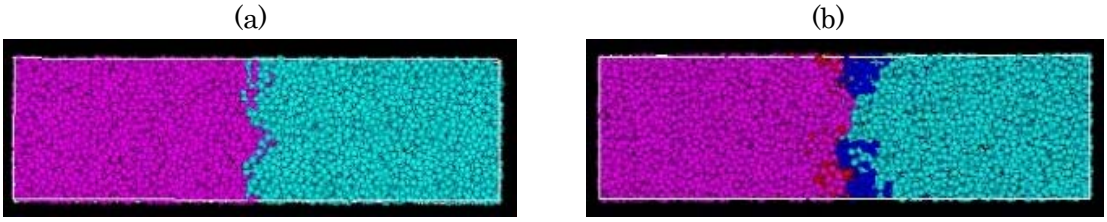

Figure 7 Snapshot structure of the interface of polymer blends, (a) A100/B100, (b) A100/A50B50/B100.

Stress-strain behavior was studied by elongating the unit cell during the coarse-grained MD simulation. Figure 8 shows an example of stress-strain curve and snapshot structure at specified strain. In this system, the fracture of interfaces was observed at around 4% strain.

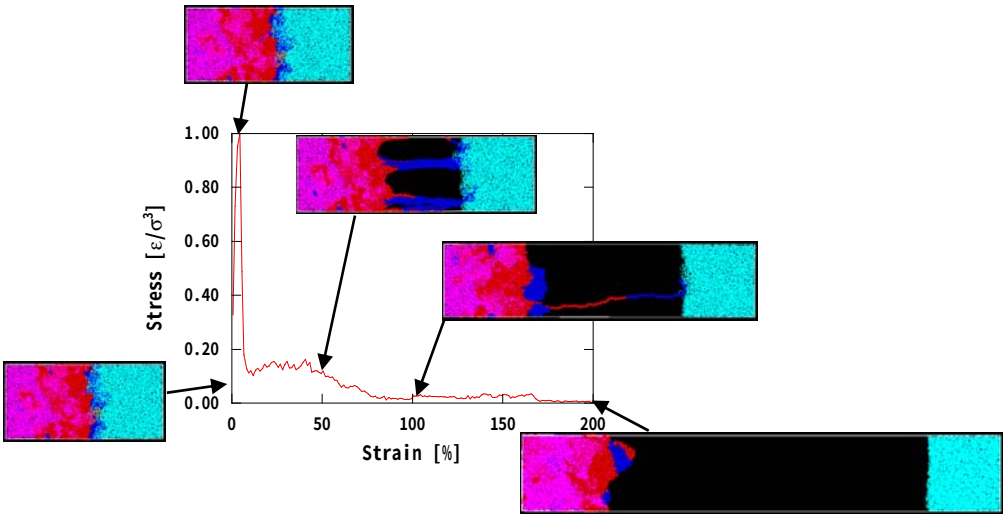

Figure 8 Stress-strain curve of the interface of polymer blend with diblock copolymer (A120/A120B30/B120) system. Inserted picture is snapshots at specified strain.

The fracture energy was calculated by integrating the stress during elongation until the interfaces were completely separated. Figure 9 shows the fracture energy as a function of surface density of block copolymers.

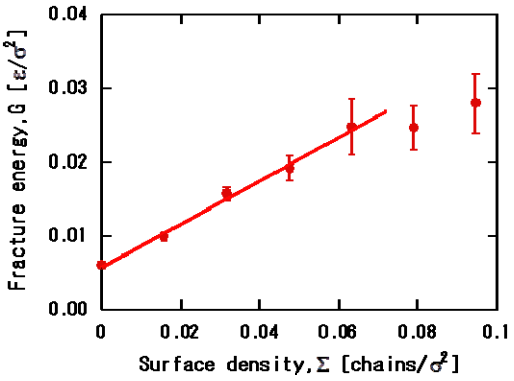

Figure 9 Fracture energy as a function of surface density of diblock copolymer.

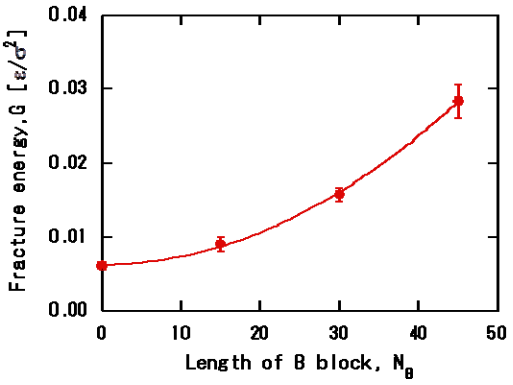

Figure 10 Fracture energy as a function of the length of shorter block.

We found that the fracture energy was proportional to the volume fraction of block copolymer until the interface was saturated with block copolymers. Figure 10 shows the interfacial energy as a function of the length of shorter block of copolymers, which is pulled out from the homopolymer phase. The fracture energy was proportional to the square of the length of the shorter block of the copolymer. These results were consistent with experimental results[7] and theoretical predictions concerning the "pull-out" region[8],

where one block of diblock copolymers was short enough not to become entangled.

4. Summary and current problems to be solved

The OCTA project was thought to be succeeded as a first step of multiscale modeling of polymer materials. However, we still need to enhance the science and technology to conduct multiscale modeling, which truly contributes the polymer material design in industry. We show some examples, which are current problems to be solved in the field of polymer modeling in the following;

(1) Large scale computing

Even though we use coarse-grained model, we still need large scale computing to handle the realistic length scale and time scale. In addition to hardware, we need effective software such as massively parallelized code running on high performance hardware.

(2) Effective coarse-graining

Coarse-graining usually loses the chemical details. However, the industrial researches often require the detail of chemical structure for material design. Thus we need more general and quantitative coarse-graining method to reproduce the structure and properties of materials originated from chemical structures.

(3) Quantitative analysis of complex morphology

Self-assembly structure shows complex morphology especially in the case of complex and non-equilibrated system. We need quantitative analysis for such a complex morphology to study the relation between structures and properties.

(4) Boundary conditions for multi scale modeling

When we try to connect two computational model of different length scale, it's always problem how to transfer the boundary condition of small system to large system especially in the case of particle model. Periodic boundary condition is a simple boundary condition. However, we can't directory put small systems with periodic boundary condition into large system, which has gradient of fields in a large scale.

We belieave that many of the problems are not pecific for polymer materials, but also for general computatioal simulation and mathematical science. Thus, we hope that we would make progress to overcome the peoblems with the collobaration of physics, chemistry and mathematical science.

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