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博 士 論 文 概 要

論 文 題 目

Construction of Polymer Ultrathin Films with Nanostructures as a Model for Biological Soft Matter Systems

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Soft matter is a material that displays solid-like properties but is distinct from traditional materials in that it is more deformable and liquid-like. Interesting behaviors arising from soft matter have become a challenging topic in material science. A number of biosystems are classifiable as soft matter, such as biomacromolecules, cell membrane, protein composite, etc., which usually present particular nanoscale structures. Fundamental understanding of the dynamical and mechanical properties of soft matter is important for bioscience and biomedical applications. However, owing to the complexity of biosystems, current experimental approach still has its limitations.

There were a large number of studies which have proven that the polymer ultrathin films possess some unique properties of soft matter, such as flexibility, adhesiveness and permeability, which are different from those of bulk polymer films. In order to mimic the multi-component biomembrane by polymer ultrathin films, the control of nanostructure is crucial due to the strong influence of morphology to properties and performances. Herein in this thesis, the author focuses on the methodology to construct the polymer ultrathin films with nanostructures and their possibility as a model for biological soft matter systems.

This thesis is consisted of six chapters. Chapter 1 deals with some core principles of soft matter and polymer ultrathin films. As the major features of soft matter, complexity and flexibility was discussed foremost. In particular, biosystems, such as cell membrane system were emphasized from a viewpoint of soft matter. Then, the concept and the anomalous behaviors of polymer ultrathin films were introduced. The author reviewed the nanofabrication technologies for construction of nanostructured polymer films, especially focusing on polymer phase separation based self-assembly technology. The basic principles of phase separation behavior of polymer blend or block copolymer were also described in this chapter.

In Chapter 2, the author established the polymer blend phase separation assisted construction method to prepare ultrathin films with nanostructures and proposed a mechanism of their formation. Typically, polymer ultrathin films were prepared by spin-casting a polystyrene (PS)/poly(methyl methacrylate) (PMMA) blend onto a poly(vinyl alcohol) (PVA)-coated silicon wafer substrate. PVA was introduced as a sacrificial layer to achieve a freestanding state. The thickness of the films could be adjusted in the range from ca. 40 to ca. 110 nm. The effect of preparation conditions, such as blend composition and rotating speed on the phase separation morphology was analyzed quantitatively. The nanoporous structure was observed after selective removing the phase separated PS regions, which embedded in the PMMA matrix. The diameter of nanopores could be adjusted in the range from ca. 60 to ca. 200 nm and was strongly dependent on the amount of PS component in blend and decreased with increasing the rotating speed.

The evolution of the morphological structure within spin-cast polymer blend ultrathin films was investigated by a solvent etching technique in combination with a freestanding method. A correlation between the film thickness and the pore size showed that in order to prepare a perforated nanoporous ultrathin film, the film thickness ought to be decreased to a level comparable to the dimensional scale of the phase separation domains, typically less than half of the diameter of the PS droplets. A simple model was proposed for the phase separation mechanism within ultrathin films during spin-casting, illustrating that the spinodal decomposition mechanism plays an important role in determining the final morphology.

In Chapter 3, the author developed a series of simple and fast methods to prepare polymer ultrathin film with porous structures based on a polymer-polymer phase separation method, such as polymer-poor solvent method, polymer-inorganic salt method and nanoparticle-patterned substrate method. The methodology proposed in this study was proven as an effective and versatile way to acquire various nanostructures. The shape, size, density, aspect ratio and even the proportion of nanostructures penetrating the film could be easily controlled by these methods, which definitely raised the possibility the resulting polymer ultrathin films to be applied as a model to mimic the diversity of complex biosystems, especially the biomembrane system.

Regarding to the application of nanostructures within polymer ultrathin film, the perforated films with uniform nanoporous structure after solvent etching are proposed as a good candidate for high flux biofilter membrane. As an example, the biocompatible poly(lactic acids) (PLA) based nanoporous films were prepared by various construction methods. The thickness of the films could be adjusted in the range from ca. 25 to ca. 600 nm and the diameter of nanopores with controllable density and distribution from tens of nanometer to microscale have been fabricated. Moreover, the freestanding method was clarified to be an efficient means of transferring the ultrathin film from the solid substrate to various other surfaces, such as human skin and animal organs.

In Chapter 4, the author discussed the basic principles of tapping mode atomic force microscopy (AFM) and introduced a technique to confirm the energy dissipation between tip-sample interaction during AFM scan. In tapping mode AFM, the tip is excited at a frequency close to its resonance value with free oscillation amplitude and approaches towards the sample until the amplitude reaches a set point value. An AFM image is mapped while the amplitude is kept at a set point value. In this study, by using the viewpoint of energy conservation, the energy input into the cantilever and tip must be equal to the energy dissipated by cantilever and tip. It is possible to calculate the average power dissipated by the tip-sample interaction by measuring the amplitude and phase shift, i.e. the force curve. As to soft matter observation with tapping mode AFM, it is reasonable to assume that the magnitude of surface deformation could be directly related to the magnitude of energy loss in the tip-sample interaction.

In Chapter 5, the author demonstrated the correlation between the soft matter surface deformation and energy dissipation during AFM scan. In order to confirm this issue, PS/PMMA blend ultrathin films as a soft matter model were chosen to investigate how certain the operation parameters of tapping mode AFM scan influenced the deformation of soft matter surface. In most cases, the thickness of the films was ca. 30nm and the diameter of PS droplets was ca. 110 nm, embedded in a matrix of PMMA. By altering the operation parameters, such as the set point value, drive amplitude, drive frequency and even the number of scan, deformation of ultrathin film could be achieved in a controllable manner. It was found the PS droplets were squeezed out of the PMMA matrix due to the interaction between tip and sample surface, moreover, the location of this deformation was limited only to the PS regions.

The average height of squeezed PS droplets was obtained by gray histogram to describe the deformation as a quantitative index. The energy dissipation between tip and PS regions was calculated and found to be controllable in this work. The power dissipation could be adjusted below ca. 50 pW over a complete tapping period. The correlation of PS droplets deformation and energy derived from tapping mode AFM tip was established and found that the magnitude of deformation increased with increasing the energy input into the system. Moreover, this energy dependence of deformation was proven to satisfy the additivity rule, i.e. the magnitude of deformation would increase with increasing the number of scan at a proper energy input.

The conclusions and future prospects of this thesis are summarized in Chapter 6. The author described a tentative exploration on construction of polymer ultrathin films with nanostructures as a model for biological soft matter systems. In the first part, fundamental methodology to construct polymer ultrathin films with nanostructures was established. As supportive information to our construction method, morphological structure evolution within spin-cast polymer blend ultrathin films was proposed, which was expected to play an important role in the formation of desired nanostructure. In the second part, based on the development of AFM theory, the deformable property of soft matter was systemically studied and the linear correlation of deformation response and energy dissipation was confirmed.

Further work is necessary to apply our nanostructured polymer ultrathin film system for bioscience and biomedical applications. The well-controlled nanostructures obtained in this work will be applicable for construction of the building blocks for the tissue engineering. Moreover, biocompatible material based nanoporous films are proposed as a good candidate for biodevice *in vivo* study. As a model for biological soft matter systems, a phospholipid-containing polymer ultrathin film will develop a model to study the lipid behavior in a simple way, instead of a complex cell membrane. The author is convinced that the polymer ultrathin films with nanostructures would be an innovative experimental model for biological soft matter systems in both theoretical research and practical applications.

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②	Hong Zhang, Yukio Honda, Shinji Takeoka. "Controllable Deformation of Nanostructured Polymer Surface with Atomic Force Microscopy", (submitted)
講演	
1	Hong Zhang, Shinji Takeoka. "Preparation of Freestanding Ultrathin Films with Uniform Nanopores by Polymer Phase Separation" *2nd Workshop for Diamond Researchers*, Tokyo, 2012.2
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その他	
1	「高分子超薄膜の製造方法及び高分子超薄膜の製造装置」, 特願 2011-105544
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