PRIOR ART DOCUMENTS

[Patent Documents]

[0008] [Patent Document 1] WO2006/025592

[Patent Document 2] WO2008/050913

[Patent Document 3] Japanese Unexamined Patent Application Publication No. 2003-155365

[Patent Document 4] Japanese Unexamined Patent Application Publication (Translation of PCT) No. 2004-502554

[Patent Document 5] Japanese Unexamined Patent Application Publication No. 2004-124088

[Patent Document 6] Japanese Unexamined Patent Application Publication No. 2010-116463

[Patent Document 7] Japanese Unexamined Patent Application Publication No. 2006-70254

[Patent Document 8] Japanese Unexamined Patent Application Publication No. 2011-105780

[Patent Document 9] Japanese Unexamined Patent Application Publication No. 2010-138286

[Patent Document 10] Japanese Unexamined Patent Application Publication No. 2009-256592

[Patent Document 11] Japanese Unexamined Patent Application Publication No. 2004-502554

SUMMARY OF THE INVENTION

Problem to be solved by the Invention

[0009] Embodiments of the present invention provide a free-standing porous ultra-thin polymer film, a method for producing a porous ultra-thin polymer film and the like.

Means for Solving the Problem

[0010] In order to solve the above-described problem, the present inventors have gone through intensive studies and in consequence conceived that a porous polymer can be produced by mixing a polymer solution with a poor solvent which is compatible with the solvent for the polymer solution and whose boiling point is higher than that of said solvent for the polymer solution, casting the resultant on a substrate to obtain an ultra-thin polymer film that has been phase-separated into a sea-island structure, and further evaporating the

poor solvent making up the island parts, and that alternatively a porous ultra-thin polymer film can be produced by dissolving two types of polymers that are mutually immiscible in solid states in a common solvent, casting the resultant on a substrate to obtain an ultra-thin polymer film that has been phase-separated into a sea-island structure and treating it with a good solvent for the polymer making up the island parts so that only the island parts are removed from the ultra-thin polymer film, thereby accomplishing embodiments of the present invention.

[0011] Specifically, embodiments of the present invention provide the following free-standing porous ultra-thin polymer film and a method for producing the same.

Disclosed herein is a free-standing porous ultra-thin polymer film having a film thickness of 10 nm-1000 nm.

In an embodiment, in the above porous ultra-thin polymer film, the pores with a size of 30 nm-50 μm are present on the surface at a density of 5 x 10-3 pores/μm2-50 pores/μm2.

In an embodiment, in the above porous ultra-thin polymer film, the size of the pores is in a range that is larger than 1 μm and smaller or equal to 25 μm.

In an embodiment, in the above porous ultra-thin polymer film, the size of the pores is in a range that is smaller or equal to 15 μm.

In an embodiment, in the above porous ultra-thin polymer film, the pore diameter distribution is at least ±20%.

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In an embodiment, in the above porous ultra-thin polymer film, the ratio of the pore diameter to the film thickness of the porous ultra-thin polymer film (pore diameter (μm)/film thickness (μm)) is 0.1-50.

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In an embodiment, in the above porous ultra-thin polymer film, the polymer is at least one selected from the group consisting of polyhydroxyalkanoic acid, a copolymer of polyhydroxyalkanoic acid, poly(ester-ether), a polyester of aliphatic dicarboxylic acid and aliphatic diol, polyamide, polyurethane, polysaccharide ester, poly(acrylate), poly(methacrylate), polystyrene, polyvinyl acetate and polysiloxane.

In an embodiment, in the above porous ultra-thin polymer film, the polymer is at least one selected from the group consisting of polyhydroxyalkanoic acid, a copolymer of polyhydroxyalkanoic acid, poly(ester-ether), a polyester of aliphatic dicarboxylic acid and aliphatic diol, polyamide, polyurethane, polysaccharide ester, poly(acrylate), poly(methacrylate), polystyrene, polyvinyl acetate and polysiloxane.

Disclosed herein is a method for producing a porous ultra-thin polymer film, comprising the steps of:

dissolving two types of mutually-immiscible polymers in a first solvent in an arbitrary proportion to obtain a solution;

applying the resulting solution onto a substrate and then removing the first solvent from the solution applied onto the substrate to obtain an ultra-thin polymer film that has been phase-separated into a sea-island structure; and

immersing the ultra-thin polymer film in a second solvent which is a good solvent for the polymer of the island parts but a poor solvent for the polymer other than the island parts to remove the island parts, thereby obtaining a free-standing porous ultra-thin polymer film with a film thickness of 10 nm-1000 nm.

In an embodiment, in the above method, the island parts of the sea-island structure have a size in a range that is larger than 1 μm and smaller or equal to 25 μm, and are present on the surface at a density of 5×10^{-3} pores/μm^2-50 pores/μm^2.

In an embodiment, in the above method, the size of the island parts of the sea-island structure is in a range that is smaller or equal to 15 μm.

In an embodiment, in the above method, the film thickness of the ultra-thin polymer film is 10 nm-1000 nm.

In an embodiment, in the above method, the combination of the first polymer forming the island parts of the sea-island structure and the second polymer forming the sea parts is selected from the following group:

(i) first polymer: polystyrene, and second polymer: polymethyl methacrylate;

(ii) first polymer: polystyrene, and second polymer: poly-D/L-lactic acid;

(iii) first polymer: polymethyl methacrylate, and second polymer: polystyrene;

(iv) first polymer: polyethylene glycol, and second polymer: polystyrene;

(v) first polymer: polyvinylpyrrolidone, and second polymer: polystyrene; and

(vi) first polymer: poly-D/L-lactic acid, and second polymer: polystyrene.

Disclosed herein is a method for producing a porous ultra-thin polymer film comprising the steps of:

dissolving a polymer as a raw material in a mixed solvent containing arbitrary proportions of a good solvent for said polymer and a poor solvent whose boiling point is higher than that of said good solvent to obtain a solution; and

applying the resulting solution onto a substrate and removing the mixed solvent from the solution applied onto the substrate to obtain a free-standing porous ultra-thin polymer film having a film thickness of 10 nm-1000 nm.

Disclosed herein is a method for producing a free-standing porous ultra-thin polymer film having a film thickness of 10 nm-1000 nm, the method comprising the steps of:

dissolving a polymer in a solvent to obtain a solution;

applying the solution onto a textured substrate and then removing the solvent from the solution applied onto the substrate to obtain an ultra-thin polymer film;

removing the textured substrate by dissolving it with a solvent that does not dissolve the ultra-thin polymer film.

In an embodiment, in the above method, the textured substrate is a substrate having a polymer thin film having dispersed and fixed microparticles, and wherein the solvent is removed from the solution applied onto the substrate to obtain an ultra-thin polymer film and then the substrate having the polymer thin film with the dispersed and fixed microparticles is removed by dissolving it in a solvent that does not dissolve the ultra-thin polymer film to obtain a porous ultra-thin polymer film.

In an embodiment, in the above method, the microparticles are at least one type of particles selected from the group consisting of polystyrene particles, silica particles, dextran particles, polylactic acid particles, polyurethane microparticles, polyacrylic particles, polyethyleneimine particles, albumin particles, agarose particles, iron oxide particles, titanium oxide microparticles, alumina microparticles, talc microparticles, kaolin microparticles, montmorillonite microparticles and hydroxyapatite microparticles.

In an embodiment, in the above method, the microparticles have a diameter of 20 nm-3000 nm.

Disclosed herein is a method for producing a porous ultra-thin polymer film comprising the steps of:

dissolving a polymer in a solvent to obtain a solution;

dispersing microparticles in the solution to obtain a dispersion;

applying the dispersion onto a substrate and then removing the solvent from the dispersion applied onto the substrate to obtain an ultra-thin polymer film; and

immersing the resulting ultra-thin polymer film in a solvent that is capable of dissolving the microparticles to remove the microparticles, thereby obtaining a free-standing porous ultra-thin polymer film with a film thickness of 10 nm-1000 nm.

In an embodiment, in the above method, the microparticles are at least one type selected from the group consisting of inorganic salts, silica, talc, kaolin, montmorillonite, polymers, metal oxides and metals.

Disclosed herein is a method for producing a porous ultra-thin polymer film comprising the steps of:

heating an ultra-thin polymer film built on a substrate to a glass-transition temperature or higher; and then compressing the ultra-thin polymer film with a separately prepared textured substrate, thereby obtaining a free-standing porous ultra-thin polymer film with a film thickness of 10 nm-1000 nm.

Disclosed herein is a method for producing a porous ultra-thin polymer film comprising the steps of: dissolving a polymer as a raw material to obtain a solution; dispersing microbubbles in the resulting solution; applying the microbubble-dispersed solution onto a substrate; and

removing the solvent from the solution applied onto the substrate, thereby obtaining a free-standing porous ultra-thin polymer film with a film thickness of 10 nm-1000 nm.

Disclosed herein is a complex of a substrate, a water-soluble sacrificial film and a porous ultra-thin polymer film, comprising the water-soluble sacrificial film on the substrate, and the above porous ultra-thin polymer film thereon.

Disclosed herein is a complex of a substrate, a water-soluble sacrificial film and a porous ultra-thin polymer film, comprising the water-soluble sacrificial film on the substrate, and the above porous ultra-thin polymer film thereon.

Disclosed herein is a complex of a substrate, a porous ultra-thin polymer film and a water-soluble support membrane, comprising the above porous ultra-thin polymer film on the substrate, and further the water-soluble support membrane on the porous ultra-thin polymer film.

Disclosed herein is a complex of a substrate, a porous ultra-thin polymer film and a water-soluble support membrane, comprising the above porous ultra-thin polymer film on the substrate, and the water-soluble support membrane on the porous ultra-thin polymer film.

Disclosed herein is a complex of a porous ultra-thin polymer film and a water-soluble support membrane, comprising the water-soluble support membrane on the above porous ultra-thin polymer film.

Disclosed herein is a complex of a porous ultra-thin polymer film and a water-soluble support membrane, comprising the water-soluble support membrane on the above porous ultra-thin polymer film.

Disclosed herein is a method for producing a free-standing porous ultra-thin polymer film comprising the step of removing the water-soluble sacrificial film or the water-soluble support membrane of the above complex with water to obtain a porous ultra-thin polymer film in water.

Disclosed herein is a method for producing a free-standing porous ultra-thin polymer film comprising a step of removing the water-soluble sacrificial film or the water-soluble support membrane of the above complex with water to obtain a porous ultra-thin polymer film in water.

In an embodiment, the method for producing the above porous ultra-thin polymer film further comprises the steps of: picking up and placing the porous ultra-thin polymer film on another substrate; and removing water from the picked up porous ultra-thin polymer film to obtain a porous ultra-thin polymer film in a dry state.

In an embodiment, the method for producing the above porous ultra-thin polymer film further comprises the steps of: picking up and placing the porous ultra-thin polymer film on another substrate; and removing water from the picked up porous ultra-thin polymer film to obtain a porous ultra-thin polymer film in a dry state.

Disclosed herein is a complex of a mesh and a porous ultra-thin polymer film, comprising the above porous ultra-thin polymer film on the mesh.

Disclosed herein is a complex of a mesh and a porous ultra-thin polymer film, comprising the above porous ultra-thin polymer film on the mesh.

Disclosed herein is a method for producing a complex of a mesh and a porous ultra-thin polymer film, comprising a step of picking up a free-standing porous ultra-thin polymer film produced by the above method with the mesh to produce a complex of the porous ultra-thin polymer film and the mesh.

Disclosed herein is a method for producing a complex of a mesh and a porous ultra-thin polymer film, comprising a step of picking up a free-standing porous ultra-thin polymer film produced by the above method with the mesh to produce a complex of the porous ultra-thin polymer film and the mesh.

Disclosed herein is a complex of a porous ultra-thin polymer film and a nonporous ultra-thin polymer film, comprising one or more of the above porous ultra-thin polymer films and one or more nonporous ultra-thin polymer films.

Disclosed herein is a complex of a porous ultra-thin polymer film and a nonporous ultra-thin polymer film, comprising one or more of the above porous ultra-thin polymer films and one or more nonporous ultra-thin polymer films.

In addition, embodiments of the present invention provide the following ultra-thin polymer film that has been phase-separated into a sea-island structure.

According to an aspect of the present invention, there is provided an ultra-thin polymer film that has been phase-separated into a sea-island structure obtained, on a sacrificial film over a substrate, by: dissolving two types of mutually-immiscible polymers, namely, a first polymer which forms island parts and a second polymer which forms parts other than the island parts, in a solvent in an arbitrary proportion to obtain a solution; applying the resulting solution onto the sacrificial film over the substrate; and then removing the solvent from the solution applied onto the sacrificial film over the substrate to form the ultra-thin polymer film, wherein the island parts of the sea-island structure have a size in a range that is larger than 1 μm and smaller or equal to 25 μm, and are present on the surface at a density of 5×10^{-3} islands/μm^2-50 islands/μm^2, and wherein the film thickness of the ultra-thin polymer film is 10 nm-1000 nm.

Here, the "first polymer" refers to a polymer that forms the island parts upon phase separation into the sea-island structure while the "second polymer" refers to a polymer that forms parts other than the island parts (sea parts).

According to another aspect, there is provided an ultra-thin polymer film that has been phase-separated into a sea-island structure obtained, between a water-soluble support film and a substrate, by: dissolving two types of mutually-immiscible polymers, namely, a first polymer which forms island parts and a second polymer which forms parts other than the island parts, in a solvent in an arbitrary proportion to obtain a solution; applying the resulting solution onto the substrate; removing the solvent from the solution applied onto the substrate to form the ultra-thin polymer film; and then providing the water soluble support film over the ultra-thin polymer film, wherein the island parts of the sea-island structure have a size in a range that is larger than 1 μm and smaller or equal to 25 μm, and are present on the surface at a density of 5×10^{-3} islands/μm^2-50 islands/μm^2, and wherein the film thickness of the ultra-thin polymer film is 10 nm-1000 nm.

In an embodiment, in the above ultra-thin polymer film, the size of the pores is in a range that is smaller or equal to 15 μm.

In an embodiment, in the above ultra-thin polymer film, the combination of the first and second polymers is selected from the group below:

(i) first polymer: polystyrene, and second polymer: polymethyl methacrylate;

(ii) first polymer: polystyrene, and second polymer: poly-D/L-lactic acid;

(iii) first polymer: polymethyl methacrylate, and second polymer: polystyrene;

(iv) first polymer: polyethylene glycol, and second polymer: polystyrene;

(v) first polymer: polyvinylpyrrolidone, and second polymer: polystyrene; and

(vi) first polymer: poly-D/L-lactic acid, and second polymer: polystyrene.

Embodiments of present invention also provide the following substantially disk-like ultra-thin polymer film (herein, sometimes referred to as a "nanodisc") and a method for producing the same.

Disclosed herein is a substantially disk-like ultra-thin polymer film whose film thickness is 10 nm-1000 nm and whose size is in a range of 30 nm-50 μm.

In an embodiment, in the above substantially disk-like ultra-thin polymer film, the size is in a range that is larger than 1 μm and smaller or equal to 25 μm.

In an embodiment, in the above substantially disk-like ultra-thin polymer film, the size is in a range that is smaller or equal to 15 μm.

In an embodiment, in the above substantially disk-like ultra-thin polymer film, the polymer is poly-D/L-lactic acid.

Disclosed herein is a method for producing a substantially disk-like ultra-thin polymer film comprising the steps of:

dissolving two types of mutually-immiscible polymers in a first solvent in an arbitrary proportion to obtain a solution;

applying the resulting solution onto a substrate and then removing the first solvent from the solution applied onto the substrate to obtain an ultra-thin polymer film that has been phase-separated into a sea-island structure; and

immersing the ultra-thin polymer film in a second solvent which is a good solvent for the polymer of the sea parts but a poor solvent for the polymer other than the sea parts to remove the sea parts, thereby obtaining a substantially disk-like ultra-thin polymer film with a film thickness of 10 nm-1000 nm and a size in a range of 30 nm-50 μm.

EFFECT OF THE INVENTION

[0014] Embodiments of present invention are capable of providing a free-standing porous ultra-thin polymer film and a method for producing the same.

BRIEF DESCRIPTION OF DRAWINGS

[0015] [Figure 1] AFM images of PS/PMMA blend nanosheets that were prepared at a rotation speed of 5000 rpm. Images after the film formation (top row), the top surfaces after the treatment with the solvent (middle row), and the back surfaces after the treatment with the solvent (bottom row). PS:PMMA (w/w) were 0:10 (left column), 1:9 (second column), 2:8 (third column) and 3:7 (fourth column).

[Figure 2] AFM images of PS/PMMA blend nanosheets that were prepared with PS:PMMA (w/w) in 2:8. Images after the film formation (top row), the top surfaces after the treatment with the solvent (middle row), and the back surfaces after the treatment with the solvent (bottom row). Rotation speeds (rpm) were 1000 (left column), 3000 (second column), 5000 (third column) and 7000 (fourth column).

[Figure 3] SEM images of porous nanosheets obtained under the respective preparation conditions. (a) 1:9 w/w, 1000 rpm (cross-section); (b) 1:9 w/w, 5000 rpm (cross-section); (c) 2:8 w/w, 1000 rpm (cross-section); (d) 2:8 w/w, 5000 rpm (perspective images of the top surface); and (e) 2:8 w/w, 3000 rpm (perspective images of the top surface).

[Figure 4] AFM images of PS/D,L-PLA blend nanosheets prepared with PS:D,L-PLA (w/w) in 3:7. Images after the film formation (top row) and the surfaces after the treatment with the solvent (bottom row). Rotation speeds (rpm) were 1000 (left column), 3000 (second column), 5000 (third column) and 7000 (fourth column).

[Figure 5] AFM images of D,L-PLA porous nanosheets obtained by a method using a mixed solvent. The top and the rear surfaces with ethyl acetate: DMSO (v/v) in 100:1 (top and second rows), the top and the rear surfaces with ethyl acetate: DMSO (v/v) in 100:3 (third and fourth rows), and the top and the rear surfaces with ethyl acetate:

CLAIMS

1. An ultra-thin polymer film that has been phase-separated into a sea-island structure obtained, on a sacrificial film over a substrate, by:

dissolving two types of mutually-immiscible polymers, namely, a first polymer which forms island parts and a second polymer which forms parts other than the island parts, in a solvent in an arbitrary proportion to obtain a solution;

applying the resulting solution onto the sacrificial film over the substrate; and

then removing the solvent from the solution applied onto the sacrificial film over the substrate to form the ultra-thin polymer film,

wherein the island parts of the sea-island structure have a size in a range that is larger than 1 μm and smaller or equal to 25 μm, and are present on the surface at a density of 5×10^{-3} islands/μm^2-50 islands/μm^2, and

wherein the film thickness of the ultra-thin polymer film is 10 nm-1000 nm.

2. The ultra-thin polymer film according to Claim 2, wherein the size of the island parts of the sea-island structure is in a range that is smaller or equal to 15 μm.

3. The ultra-thin polymer film according to Claim 1 or 2, wherein the combination of the first and second polymers is selected from the group below:

(i) first polymer: polystyrene, and second polymer: polymethyl methacrylate;

(ii) first polymer: polystyrene, and second polymer: poly-D/L-lactic acid;

(iii) first polymer: polymethyl methacrylate, and second polymer: polystyrene;

(iv) first polymer: polyethylene glycol, and second polymer: polystyrene;

(v) first polymer: polyvinylpyrrolidone, and second polymer: polystyrene; and

(vi) first polymer: poly-D/L-lactic acid, and second polymer: polystyrene.

4. An ultra-thin polymer film that has been phase-separated into a sea-island structure obtained, between a water-soluble support film and a substrate, by:

dissolving two types of mutually-immiscible polymers, namely, a first polymer which forms island parts and a second polymer which forms parts other than the island parts, in a solvent in an arbitrary proportion to obtain a solution;

applying the resulting solution onto the substrate;

removing the solvent from the solution applied onto the substrate to form the ultra-thin polymer film; and then

providing the water soluble support film over the ultra-thin polymer film,

wherein the island parts of the sea-island structure have a size in a range that is larger than 1 μm and smaller or equal to 25 μm, and are present on the surface at a density of 5×10^{-3} islands/μm^2-50 islands/μm^2, and

wherein the film thickness of the ultra-thin polymer film is 10 nm-1000 nm.

5. The ultra-thin polymer film according to Claim 4, wherein the size of the island parts of the sea-island structure is in a range that is smaller or equal to 15 μm.

6. The ultra-thin polymer film according to Claim 4 or 5, wherein the combination of the first and second polymers is selected from the group below:

(i) first polymer: polystyrene, and second polymer: polymethyl methacrylate;

(ii) first polymer: polystyrene, and second polymer: poly-D/L-lactic acid;

(iii) first polymer: polymethyl methacrylate, and second polymer: polystyrene;

(iv) first polymer: polyethylene glycol, and second polymer: polystyrene;

(v) first polymer: polyvinylpyrrolidone, and second polymer: polystyrene; and

(vi) first polymer: poly-D/L-lactic acid, and second polymer: polystyrene.