Abstract: The present invention relates to a preparation method of copolymer between phosphorylcholine monomer and epoxy monomer, and its application to surface coating material using the resulting copolymer. Specifically, by using a monomer having an epoxy group as a monomer being copolymerized with phosphorylcholine monomer, a mechanical and chemical stability of the polymer resin can be further improved, and also, no swelling may occur when the polymer is impregnated with water. Thus it can be used as a coating agent for a sensor device or biomedical materials etc., due to its excellent ability to permeate oxygen.
Anti-fouling copolymer resin

[Technical Field]

The present invention relates to a method of preparing copolymer resin comprising phosphorylcholine groups which inhibits an adhesion of microorganisms, and to coating materials prepared in accordance with such method. When the resin of the present invention is used as a composition for coating, adhesion of the microorganisms on film surface is minimized and cross-linking between epoxy groups present in the polymers is induced, and therefore, the physical property of the coatings is improved.

[Background Art]

There has been a method of using N-halamine polymer, fluoroalkyldiol-comprising material, or plasma-treated polymer, in order to solve the problems relating to adhesion of microorganisms which cause a reduction in lifetime and sensitivity of a sensor. However, such methods are disadvantageous since they require a complicated process to prepare, and the product produced in accordance with the method exhibits an antibacterial effect and hydrophobicity which can cause peel-off of coated surface due to unsatisfactory adhesion or mechanical property. Hence, many studies have been carried out to develop the methods that can
prevent the adhesion of the microorganisms. It was found that the use of a polymer comprising phosphorylcholine groups yields a coating surface with the most effective anti-fouling effect. However, when such a polymer comprising phosphorylcholine groups with low molecular weight is applied to a sensor, its poor mechanical property causes a problem of weak physical bonding and instability. In addition, when the sensor is used for a long period of time, a swelling problem occurs due to absorption of water by the polymer. Thus, in order to apply the phosphorylcholine groups to the field of coating, a modification of the polymer is needed so that it can have preferable mechanical and chemical properties, so as to be stably applied to surface of a substrate.

[Disclosure]

[Technical Problem]

In order to solve the problems described above, the present invention provides a method of preparing an anti-fouling copolymer by copolymerizing a monomer having a phosphorylcholine group and a monomer having an epoxy group, and the resulting copolymer is used as a coating agent for a sensor, etc. Preparation and application of the above copolymer constitutes the object of the present invention.

More specifically, the object of the present invention is to provide a composition for coating which has an anti-fouling
property with improved solvent and chemical stability, and an improved mechanical property such as low-shrinkage and adhesion, etc., by introducing phosphorylcholine and epoxy groups to the polymer.

The present invention is based on the finding that, anti-fouling coating surface having excellent physical and chemical properties can be produced by preparing a copolymer having an epoxy and a phosphorylcholine groups. The resulting copolymer is applied to a substrate to form a coating surface, and cross-linking the polymer at relatively low temperature using an amine compound as a catalyst. Thus, the obtained coating can be successfully applied to a sensor or biomedical materials.

[Technical Solution]

The present invention aiming to solve the problems described above has an object of avoiding adhesion on the surface of a substrate which requires no adhesion by microorganisms and proteins. Thus, the present invention relates to the preparation of copolymer containing phosphorylcholine and epoxy groups, and its application to a material for antifouling surface coating.

According to the present invention, phosphorylcholine monomer plays a role of inhibiting adhesion of microorganisms and proteins, and when a polymer comprising phosphorylcholine
monomer is used as a coating material, the adhesion of microorganisms and proteins to the surface of the substrate can be prevented, and therefore, such substrate can be successfully used for a sensor or biomedical materials. In addition, epoxy monomer plays a role of improving a physical property of the polymer, because the copolymer, obtained by cross-linking of epoxy groups with heating, has a better mechanical and chemical properties compared to conventional polymer films. Hence, the copolymer resin prepared according to present invention can be widely applied to a sensor or biomedical materials. Especially when a small amount of an amine compound is employed as a catalyst for cross-linking of epoxy groups in polymer, the solution of which is coated to a surface of substrate, and then treated with heat, more effective cross-linking can be achieved at relatively low temperature and stability of the resulting film can be greatly improved.

Specifically, by using a monomer having an epoxy group as a monomer being copolymerized with phosphorylcholine monomer, a mechanical and chemical stability of the polymer resin can be further improved, since no swelling may occur when the polymer is impregnated with water. Thus it can be used as a coating agent for a sensor device or biomedical materials, etc., due to its excellent ability to permeate oxygen.

More specifically, the present invention relates to an
anti-fouling copolymer resin comprising structural unit 1 and structural unit 2 described below.

[Structural unit 1]

\[
\begin{align*}
\text{COOR}_2
\end{align*}
\]

[Structural unit 2]

\[
\begin{align*}
\text{COOR}_4 \text{O} \text{P} \text{O} \text{R}_5 \text{N}^{\ominus} \text{R}_7 \text{R}_8
\end{align*}
\]

(wherein \(R_1\) and \(R_3\) are hydrogen or alkyl groups having from 1 to 5 carbon atoms and independent each other. \(R_2\), \(R_4\), \(R_5\), \(R_6\), \(R_7\), and \(R_8\) are a hydrogen or alkyl groups having from 1 to 20 carbon atoms and independent each other.)

Even more specifically, the present invention relates to an anti-fouling copolymer resin having chemical formula 1 below.

[Chemical formula 1]

\[
\begin{align*}
\text{COOR}_2 \text{H}_2 \text{C} \text{R}_1 \text{R}_3 \text{COOR}_4 \text{O} \text{P} \text{O} \text{R}_5 \text{N}^{\ominus} \text{R}_7 \text{R}_8
\end{align*}
\]

(wherein \(R_1\) and \(R_3\) are hydrogen or alkyl groups having from 1 to 5 carbon atoms and independent each other. \(R_2\), \(R_4\), \(R_5\), \(R_6\), \(R_7\), and \(R_8\) are hydrogen or alkyl groups having from 1 to 20 carbon atoms and independent each other. \(m\) and \(n\) are an
integer of 1 to 10,000 and independent each other.)

The compound of chemical formula 1 can be prepared from a phosphorylcholine derivative of Chemical formula 2 below and glycidyl (meth)acrylate.

[Chemical formula 2]

(whose R4, R5, R6, R7, and R8 are a hydrogen or alkyl groups having from 1 to 20 carbon atoms with no dependence each other.)

More preferably, previously mentioned phosphorylcholine derivative can be 2-methacryloxyethyl phosphorylcholine (MPC) of chemical formula 3 below, in terms of easier preparation of the polymer.

[Chemical formula 3]

Advantageously, the phosphorylcholine derivative is used in an amount of 0.01 to 10 parts by weight relative to 100 parts by weight of glycidyl (meth)acrylate. When more than 10 parts by weight of the phosphorylcholine derivative is used, the cross-linking may occur when the resin is stored at room
temperature due to the presence of a quaternary ammonium groups. In addition, since just a small amount of the phosphorylcholine derivative can be effective to achieve an anti-fouling effect, 0.01 to 10 parts by weight of the phosphorylcholine derivative is preferably used.

In the present invention, the phosphorylcholine derivative of the chemical formula 3 can be prepared by the known method. Further, a polymer resin having not only an anti-fouling but also an improved mechanical and chemical properties can be obtained by carrying out the copolymerization reaction between the phosphorylcholine derivative obtained from the known method and the epoxy monomer described above, and the polymer can be successfully applied to a coating material for a sensor or biomedical materials etc. without any swelling.

The method for preparing the polymer resin of the present invention comprises the following steps in detail;

1) mixing phosphorylcholine derivative of Chemical formula 3, glycidyl (meth) acrylate and an initiator; and

2) stirring the resulting mixture of step 1) at 40 ~ 80 °C for 10 ~ 30 hours for radical polymerization.
The initiator can be a radical initiator, which is used as a conventional heat initiator or reduction-oxidation initiator. For example, the initiator can be azobisisobutyronitrile (AIBN) but is not limited thereto.

The phosphorylcholine derivative of chemical formula 3 can be prepared in accordance with the method comprising the following steps:

1) adding triethylamine and 2-hydroxyethylmethacrylate to purified tetrahydrofuran and completely dissolving them to form a solution, lowering the temperature to -20 ~ -30 °C, and then slowly adding dropwise 2-chloro-2-oxo-1, 3,2-dioxapholane for an hour while stirring the solution;

2) maintaining the temperature of the mixture solution at temperature of -25 °C for four hours to proceed with the reaction;

3) after the completion of the reaction, filtering off the precipitates (triethyl ammonium chloride) present in the mixture and drying the filtrate under reduced pressure;

4) adding purified ethyl ether and distilled water to the filtrate in order to remove trace of triethyl ammonium.
chloride, and then drying the resultant under reduced pressure to obtain 2-(2-oxo-1, 3,2-dioxaphosphoroyloxy) ethyl methacrylate (OPEMA) of chemical formula 4 below as colorless liquid;

5) [Chemical formula 4]

\[
\begin{array}{c}
\text{COOCH}_2\text{CH}_2\text{O-P=O} \\
\end{array}
\]

5) dissolving the intermediate of chemical formula 4 in acetonitrile contained in a pressurized vessel, lowering the temperature of the vessel to less than -30 °C, and then adding triethylamine to the solution;

6) sealing the pressurized vessel, warming up the temperature and heating the vessel to 60 °C for 16 hours using a shaking incubator with 180 rpm, and then lowering the temperature below -20 °C to yield white precipitates; and

7) filtering thus obtained precipitates under nitrogen stream, washing them with cold acetonitrile, and drying them under the reduced pressure to provide 2-methacryloxyethyl phosphorylcholine (MPC) of the following chemical formula 3, which is a derivative of phosphorylcholine.

[Chemical formula 3]
Although 2-methacryloxyethyl phosphorylcholine, as prepared according to the published known process, was used in the present invention, a different kind of monomer having phosphorylcholine group can be also used, and it is certainly not limited to the compound of chemical formula 3 above.

The constitutional ratio for the phosphorylcholine derivatives and glycidyl methacrylate in the above-described step 1) may vary depending on specific purpose. However, it is preferable to use the phosphorylcholine derivatives in an amount of 0.01 to 10 parts by weight relative to 100 parts by weight of glycidyl methacrylate, in terms of mechanical property and processibility of the polymer resin.

The epoxy resin of the present invention, that is prepared to comprise a phosphorylcholine group, can be
dissolved in an organic solvent with diamine compounds to provide a coating material made of epoxy resin which has excellent mechanical and anti-fouling properties, as claimed for the purpose of the invention.

The amine compounds used in the present invention can be any kind of alkyl or aryl amines. Especially, the amine compounds such as diaminohexane, methylenedianiline, methylenebiscyclohexaneamine, etc. that carries more than one amine group are found to be effective in the present invention. For the solvent used in the present invention, anyone that can dissolve the reactants can be used.

It is preferable to mix from 5 to 10% by weight of the epoxy resin, from 1 to 5% by weight of the diamine compound and from 85 to 94% by weight of the organic solvent. If the epoxy resin is used above 10% by weight, resulting polymer solution becomes highly viscous and is difficult to be processed as a coating agent. Thus, in the present invention the resin mixture with appropriate viscosity is prepared by controlling the amount of the organic solvent.

The epoxy resin prepared as described above can be coated onto surface of glass, polymer, metal, ceramic and fiber, etc. After being coated onto the substrate to form a coating surface, it is heat-treated at 40 ~ 200 °C in order to induce cross-linking reaction. The mechanical and chemical properties of the polymer resin according to the present invention are
significantly improved by cross-linking reaction, and therefore the physical characteristic of an electronic device which is treated with such polymer resin can be remarkably improved, too.

The epoxy resin polymer prepared in accordance with the present invention has an anti-fouling property, and therefore can be used in various areas including biomedical materials, vehicles for drug delivery, separation membrane and a coating agent for a sensor which is employed for monitoring many variables such as pH, level of dissolved oxygen, and level of dissolved carbon dioxide, etc.

[Description of Drawings]

Figure 1 is a scanning electron microscope (SEM) photograph to determine adhesion of E. coli.

[Mode for Invention]

The present invention is illustrated in greater detail by following examples now described. However, the present invention is not limited to the examples.

[Preparation Example 1]

<Preparation of Phosphorylcholine Derivatives>

(a) Synthesis of Intermediates

Triethylamine (0.92 g; 7.1 mmol) and 2-
hydroxyethylmethacrylate (HEMA, 0.92 g; 7.1 mmol) were added to purified tetrahydrofuran (THF, 9.2 ml) and completely dissolved. The mixture was cooled down to temperature of -25 °C and then 2-chloro-2-oxo-1,3,2-dioxapholane (COP, 0.72 g; 7.1 mmol) was slowly added dropwise over an hour while stirring the mixture. After maintaining the reaction at -25 °C for three hours, precipitates (triethylammoniumchloride) were filtered off at the end of reaction and the filtrate was dried under reduced pressure. The trace left on the filter was purified by washing with purified ethylether (5 ml), and the filtrate was dried under reduced pressure to obtain 2-(2-oxo-1,3,2-dioxaphosphoroyloxy) ethyl methacrylate (OPEMA) as colorless liquid.

IH-NMR (CDCl3): δ 2.00 (s, 3H, NCH3), 3.7-4.3 (s, 8H, CH2), 5.60 (s, IH, CH=CH), and 6.20 (s, IH, CH=CH);

(b) Synthesis of phosphorylcholine derivatives (MPC)

The intermediate of Chemical formula 1 (1.0 g) which has been obtained from the above section (a) was dissolved in acetonitrile (10 ml), then after cooling the temperature to -20 °C triethylamine (0.4 ml) was added to the solution. The pressurized vessel containing the resulting solution was tightly sealed and heated at 60 °C and 180 rpm for 16 hours. Then the temperature was lowered to -20 °C again to obtain white precipitates, which were subsequently filtered under stream of nitrogen and washed with cold acetonitrile (10 ml).
After drying under reduced pressure, 2-methacryloxyethyl phosphorylcholine (MPC) was obtained.

IH-NMR (CDCl3) : \( \delta \ 2.00 \ (s, -\text{CH}_3, 3H) \), 2.7-2.9 \ (s, N(\text{CH}_3)_3, 9H) \ 3.7-4.3 \ (-\text{CH}_2-, 8H) \), 5.60 \ (-\text{CH}=, \text{IH}) \), 6.20 \ (-\text{CH}=, \text{IH}) \).

[Example 1]

Preparation of copolymer P (GMA-co-MPC) >

MPC monomer obtained from the above-described preparation example (0.05 g), glycidylmethacrylate (1.0 g) and azobisisobutyronitrile (AIBN, 10 mg) as an initiator were dissolved in 20 ml of mixed solvent comprising tetrahydrofuran (14 ml) and methanol (6 ml). After purging with nitrogen gas, the reaction vessel was sealed and stirred at 60 °C for 16 hours. After carrying out the precipitation twice with n-hexane, white polymer having molecular weight of 1.20 x 10^5 was obtained in powder form (0.86 g; Yield 82%).

[Example 2 and Example 3]

More copolymers were prepared by using the same method as described in Example 1, except that different amounts of 2-methacryloxyethylphosphorylcholine (MPC) and glycidyl methacrylate (GMA) were used as summarized in the following Table 1.
Number average molecular weight was determined using dynamic light scattering spectroscopy (Model No: DLS-8000HL, manufactured by Otsuka Electric Co.).

For the copolymers prepared according to Example 1, Example 2 and Example 3, their physical characteristics were determined based on the methods described below.

### Table 1

<table>
<thead>
<tr>
<th>Example</th>
<th>GMA (g)</th>
<th>MPC (g)</th>
<th>AIBN (mg)</th>
<th>Yield (%)</th>
<th>Number Average Molecular Weight (x 10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.00</td>
<td>0.024</td>
<td>10.0</td>
<td>78</td>
<td>0.93</td>
</tr>
<tr>
<td>3</td>
<td>1.00</td>
<td>0.036</td>
<td>10.0</td>
<td>63</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Number average molecular weight was determined using dynamic light scattering spectroscopy (Model No: DLS-8000HL, manufactured by Otsuka Electric Co.).

For the copolymers prepared according to Example 1, Example 2 and Example 3, their physical characteristics were determined based on the methods described below.

### Experimental Example 1

**determination of degree of cross-linking in copolymer film**

Each of the copolymers prepared from above Examples 1 to 3 (0.05 g) were dissolved respectively in chloroform (1 ml), and methylene biscyclohexylamine and methylenedianiline as a catalyst for cross-linking were added 2.5 mg respectively and dissolved. The resulting solution was coated onto a silicon wafer to give a film having thickness of 1.7 µm.

The film was then heat-treated at temperatures of from 40 to 140 °C and degree of cross-linking was determined for each different temperatures. As a result, it was found that when the cross-linking was carried out at temperature above 80 °C using the above-described two kinds of amine compound the cross-linking occurred at lower temperature compared to the
cross-linking without using any catalyst for cross-linking.

As a result, it was confirmed that copolymer P(MPC/GMA) can be cross-linked at relatively low temperature when it is used as a coating agent for a sensor, and therefore a more stable sensor can be produced using the copolymer resin of the present invention.

[Experimental Example 2]
Experimental comparison for transparency of copolymers>

Copolymer obtained from the above Example 1 (0.5 g) was dissolved in chloroform (10 ml) to give a solution with the polymer concentration of 5% by weight, which was then applied evenly to surface of a quartz plate (1.76 µm). Transparency of the resulting quartz plate was compared to that of polyglycidyl methacrylate (PGMA, molecular weight; 7 x 10^4).

Results are summarized in the following Table 2.

Method: the polymer was coated onto the quartz plate with 400 rpm and 1200 rpm for 10 sec and 20 sec respectively (1st and 2nd application)

Instrument for determination: UV-VIS spectrum, Jasco, Model V-550

[Table 2]

<table>
<thead>
<tr>
<th></th>
<th>Transparency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500 nm</td>
</tr>
<tr>
<td>Example 1</td>
<td>100</td>
</tr>
<tr>
<td>PGMA</td>
<td>100</td>
</tr>
</tbody>
</table>

Similar to PGMA film having typical good transparency,
the copolymer resin prepared according to the present invention had a good transparency of 90% or more for light at wavelengths longer than 300 nm.

[Experimental Example 3]

<Adhesiveness determination for the copolymers>

Each of the copolymer obtained from the above Example 1, Example 2 and Example 3 (0.2 g) was dissolved respectively in chloroform (1 ml) to give a solution with the polymer concentration of 20% by weight, and methylene biscyclohexylamine (5% by weight, 0.1 g) was added thereto. Thus obtained solution was then applied evenly to surface of a clean glass plate to have a polymer coated film with 58 µm thickness.

Resulting film was heat-treated for 20 min at 80 °C and cross stripes with a size of 1mm x 1mm were created by cutting the film with a cross hatch cutter. Then a sticky tape was applied to the cross stripes and soon peeled off. Level of peel off of the film that had been coated onto the glass plate was determined (ASTM D3359-97, "Standard test methods for measuring adhesion by tape test" Test Method B). Results are summarized in the following Table 3.

<table>
<thead>
<tr>
<th>Adhesiveness</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5B</td>
<td>5B</td>
<td>5B</td>
</tr>
</tbody>
</table>

Adhesiveness of the copolymer resin comprising epoxy
groups according to the present invention was found to be 5B, which corresponds to an excellent adhesiveness (5B described in Table 3 indicates that none of the cross stripes were peeled off).

[Experimental Example 4]

<Measurement of adhesion by microorganisms>

Each of the copolymer obtained from the above Example 1, Example 2 and Example 3 (0.05 g) was dissolved respectively in chloroform (1 ml) and methylenebiscyclohexylamine (2.5 mg) was added thereto. Thus obtained solution was then applied evenly to surface of a petri dish (1.76 µm thickness) and sterilized with irradiation by UV lamp. E.coli previously activated in liquid broth (9 µl) were inoculated with the liquid broth to the petri dish and cultured at 37 °C, 180 rpm for 6, 12, 18, 24 or 30 hours, respectively. Each plate was examined under the scanning electron microscope (Hitachi model S-4700) to determine the degree of adhesion by the microorganism to the glass plate or to the PGMA-coated plate. Results are shown in Fig. 1, in which the test results for (a) the glass plate, (b) PGMA-coated plate, (c) Example 2, (d) Example 3 and (e) Example 4 are given.

As it can be clearly seen from Fig. 1, the degree of adhesion by the microorganisms is significantly lower for the plates coated with copolymer P(MPC/GMA) prepared in accordance
with the present invention (i.e., Example 2, Example 3 and Example 4) compared to that of the glass or the PGMA-coated plates. Therefore, it is found that in light of such advantageous characteristic, the copolymer of the present invention can be used for coating the surface of a sensor which in turn can minimize the adhesion by microorganisms and therefore increase the lifetime of the sensor itself.

[Experimental Example 5]

<Derivatization with the fluorescent compound Ru-DPP using sol-gel method and measurement of oxygen permeability>

Methyltriethoxysilane (12.5% v/v) was added to ethanol (60.5% v/v), and then glycidoxy triethoxysilane (25% v/v) and aqueous HCl solution (0.5% v/v) were added to the mixture, to which a fluorescent compound Ru-DPP having chemical formula 5 was mixed in (1.5% v/v). Resulting solution was evenly applied to the surface of a quartz plate and dried at room temperature for three to four days, and then dried at 80 °C for one day.
Next, copolymer obtained from the above-described Example 1 (0.05 g) was dissolved in chloroform (1 ml) and methylene biscyclohexylamine, which is a linear diamine compound, was added thereto (5% by weight, 2.5 ml). Thus obtained solution was then filtered through a membrane filter having pore size of 0.45 µm, and the filtrate was applied to the film obtained from above Experimental Example 5 to give a coated thin film (thickness, 1.76 µm). The film was subsequently dried in oven at 80 °C. Oxygen permeability for the coated copolymer film obtained above was determined based on fluorescence spectrum taken for each concentration of oxygen gas contained in argon gas.

As a result, it was found that, as the flow rate for oxygen increases from zero (flow rate for argon gas was 1.0 ml/min), the fluorescence intensity of Ru-DPP dye decreases (see Table 4 below).
[Table 4]

<table>
<thead>
<tr>
<th>Flow rate for oxygen (L/min)</th>
<th>1.0</th>
<th>0.8</th>
<th>0.6</th>
<th>0.4</th>
<th>0.2</th>
<th>0.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence intensity (AU)</td>
<td>267.33</td>
<td>290.48</td>
<td>298.13</td>
<td>308.09</td>
<td>316.51</td>
<td>321.69</td>
</tr>
</tbody>
</table>

In view of the foregoing, it is confirmed that the copolymer of the present invention which comprises epoxy groups has an excellent adhesiveness, oxygen permeability, transparency and enhanced mechanical property, as well as anti-fouling property.

[industrial Applicability]

By comprising a phosphorylcholine group in its structure, the copolymer resin prepared according to the method of the present invention exhibits an excellent anti-fouling effect. In addition, by employing the monomer with an epoxy group, the copolymer having excellent mechanical and chemical properties can be prepared according to the method of the present invention. Also, the copolymer of the present invention can be used as a surface-coating agent in many different areas, and it can be applied to any kind of surface including glass, polymer, metal, ceramic and fiber, etc., which requires an anti-fouling property.
[CLAIMS]

[Claim 1]

Anti-fouling copolymer resin comprising Structural unit 1 and Structural unit 2 described below.

[Structural unit 1]

\[
\begin{align*}
R_1 & \quad \text{CH}_2 \quad \text{C} \quad \text{COOR}_2 \\
\end{align*}
\]

[Structural unit 2]

\[
\begin{align*}
R_3 & \quad \text{CH}_2 \quad \text{C} \quad \text{COOR}_4 \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{N} \quad \text{R}_6 \\
\end{align*}
\]

(wherein \( R_1 \) and \( R_3 \) are hydrogen or alkyl groups having from 1 to 5 carbon atoms and independent each other. \( R_2, R_4, R_5, R_6, R_7, \) and \( R_8 \) are hydrogen or alkyl groups having from 1 to 20 carbon atoms and independent each other.)

[Claim 2]

The anti-fouling copolymer resin of claim 1, wherein copolymer resin has chemical formula 1 below.

[Chemical formula 1]

\[
\begin{align*}
\text{\( (\text{CH}_2 \quad \text{C})_m \quad \text{CH}_2 \quad \text{C} \quad (\text{COOR}_2 \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{N} \quad \text{R}_6) \quad \text{COOR}_4 \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{N} \quad \text{R}_7) \end{align*}
\]

(wherein \( R_1 \) and \( R_3 \) are hydrogen or alkyl groups having from 1
to 5 carbon atoms and independent each other, and R2, R4, R5, R6, R7, and R8 are hydrogen or alkyl groups having from 1 to 20 carbon atoms and independent each other, and m and n are an integer of 1 to 10,000 and independent each other.)

[Claim 3]
The anti-fouling copolymer resin of claim 2, wherein mentioned copolymer resin is prepared from a phosphorylcholine derivative of chemical formula 2 below and glycidyl (meth)acrylate.

[Chemical formula 2]

\[
\text{COOR}_4\text{PO}_3\text{R}_5\text{N}^{\ominus}\text{R}_7
\]

(wherein R4, R5, R6, R7, and R8 are hydrogen or alkyl groups having from 1 to 20 carbon atoms and independent each other.)

[Claim 4]
The anti-fouling copolymer resin of claim 3, wherein mentioned phosphorylcholine derivative, is 2-methacryloxyethyl phosphorylcholine (MPC) of chemical formula 3 below.

[Chemical formula 3]
Preparation method of anti-fouling copolymer resin comprising the following steps,-

1) mixing phosphorylcholine derivative of chemical formula 2 below, glycidyl (meth)acrylate and an initiator; and

2) stirring the resulting mixture of step 1) at 40 ~ 80 °C for 10 ~ 30 hours for radical polymerization.

[Chemical formula 2]

(wherein R4, R5, R6, R7, and R8 are hydrogen or alkyl groups having from 1 to 20 carbon atoms and independent each other.)

Anti-fouling coating material prepared by dissolving copolymer resin prepared according to the preparation method of claim 5 and diamine compound in an organic solvent.
The anti-fouling coating material of claim 6, wherein
mentioned coating material is the mixture of from 5 to 10% by
weight of the epoxy resin, from 1 to 5% by weight of the
diamine compound and from 85 to 94% by weight of the organic
solvent.

[Claim 8]
Formation method of anti-fouling coating surface comprising
the following steps;

1) coating the coating material according to claim 6 onto
the surface of substrate; and

2) heat-treating the resulting coating surface of step 1) at 40 ~ 200 °C for cross-linking reaction.

[Claim 9]
The formation method of anti-fouling coating surface of claim
8, wherein surface of substrate is the surface of one selected
from the group consisting of glass, polymer, metal, ceramic
and fiber.
INTERNATIONAL SEARCH REPORT

PCT/KR2007/001296

A. CLASSIFICATION OF SUBJECT MATTER

C08F 220/32(2006.01)i, C08F 230/02(2006.01)i, C08F 220/34(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKIPASS, Registry(STN), CA(STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
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<tr>
<td>X</td>
<td>JP2002-348779 A (NOF CORP et al.) 04 Dec 2002 Claims 1-6, Par [6]-[8], [10], [34], [47]</td>
<td>1-5</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents
  *A* document defining the general state of the art which is not considered to be of particular relevance
  *E* earlier application or patent but published on or after the international filing date
  *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
  *O* document referring to an oral disclosure, use, exhibition or other means
  *P* document published prior to the international filing date but later than the priority date claimed
  *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  *X* document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  *Y* document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  *&* document member of the same patent family

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Name and mailing address of the ISA/KR
Korean Intellectual Property Office
920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea
Facsimile No 82-42-472-7140

Authorized officer
KANG, HYUNG SEOK
Telephone No 82-42-481-5597

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