AMPHIPHILIC SILOXANE GEL AND PREPARATION METHOD THEREFOR

FIELD OF THE INVENTION

The present application relates to the field of organic materials, and specifically relates to an amphiphilic siloxane gel and a preparation method therefor.

BACKGROUND OF THE INVENTION

In order to adapt to the environmental requirements, increase the life of equipment and facilities, and protect the performance of equipment and facilities, there is a need for antifouling in many fields. Anti-fouling coatings are a commonly used means of antifouling, and have a wide range of application needs in the fields of marine engineering, chemical industry, etc. However, existing anti-fouling coating technologies often have a single application scenario, for example, self-polishing or biocidal/anti-adhesive releasing coatings are usually used in marine applications, and this type of anti-fouling method is not only involves environmental protection issues, but also can’t be used in other application scenarios except for marine environments. Although a few low-surface-energy coatings have started to be used as anti-fouling coatings, they have a single mechanism of action and usually show low anti-fouling efficiency in complex contaminated environments.

Siloxane gels have excellent heat resistance, weather resistance, oil resistance, cold resistance, electrical insulation properties while having low modulus of elasticity and low stress, as well as low cost, thus they have broad applications in both industrial and daily applications. However, the existing siloxane gel is mainly prepared by chemical cross-linking curing/sulfurization to form a network without dynamic properties, and because the raw material contains only low surface energy silanes, the resulting material is only hydrophobic, so using the existing siloxane gels as a low-surface-energy anti-fouling and anti-adhesion coatings has the following drawbacks: 1. the anti-fouling mechanism is single, and the anti-fouling and anti-adhesion performance exhibited is limited for the complex polluted environments; 2. the thermosetting network formed is not reversible, and

the coating cannot be recycled; 3. it is difficult to maintain and remove the coating after it loses its function; and 4. there is an upper limit to its anti-fouling period of validity due to its fixed lubricant content.

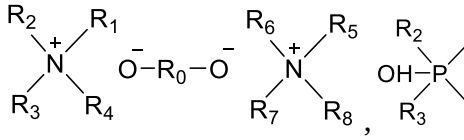
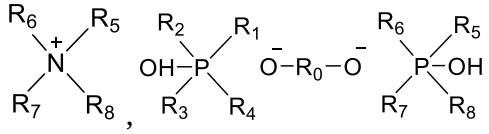
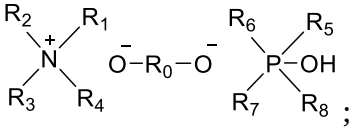
SUMMARY OF THE INVENTION

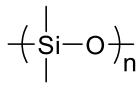
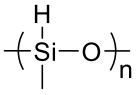
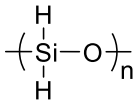
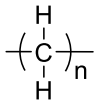
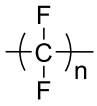
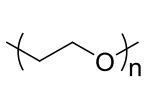
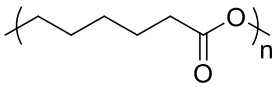
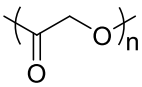
Therefore, the technical problem to be solved by the present application is to overcome the defects of siloxane gel in the prior art as an anti-fouling and anti-adhesion coating, so as to provide an amphiphilic siloxane gel and a preparation method therefor.

To this end, the present application adopts the following technical solution.

The present application provides an amphiphilic siloxane gel, the gel comprises an active species, and the active species is one of or a mixture of more of organic bases having quaternary ammonium salt groups or alkylphosphonium hydroxide groups.

Further, the organic base has one of the following structural formulae:


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, and 
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wherein R_0 is one of 
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and 
;

R_1 is C_aH_{2a+1}, R_2, R_3, R_4, R_5, R_6, R_7, and R have identical structures or a combination of different structures, which are selected from C_bH_{2b+1} and phenyl, $0<n<100$, $0<a<8$, and $0<b<20$. The amphiphilic siloxane gel described in the present application comprises the following mass parts of raw materials:

2.5-15 parts of active species

85-97.5 parts of cyclic siloxane, and

40-150 parts of lubricating fluid.

Preferably, the cyclic siloxane is one of or a combination of more of hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, cyclotetrapolydimethylsiloxane, tetramethyltetravinylcyclotetrasiloxane,

2,4,6,8-tetramethyl-2,4,6,8-tetrakis(3,3,3-trifluoropropyl)cyclotetrasiloxane, octaphenylcyclotetrasiloxane, heptamethylphenylcyclotetrasiloxane, 1,3,5,7-tetrakis(diphenylphosphinoethyl) tetramethylcyclotetrasiloxane, tetramethyltetraphenylcyclotetrasiloxane, methacryltrisepoxycyclosiloxane , tetrakisepoxy cyclosiloxane, 1,3,5,7-tetramethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, and tetradecamethylcycloheptasiloxane.

The lubricating fluid is one of or a combination of more of silicone oil derivative, fluorinated polyether oil and mineral oil, the silicone oil derivative comprises dimethyl silicone oil, phenyl silicone oil and the like, and the viscosity of the lubricating fluid is 10-1000 cst.

The present application also provides a method for preparing the amphiphilic siloxane gel described above, comprising the following steps:

S1: mixing an active species and a cyclic siloxane, and then carrying out a ring-opening polymerization to obtain a gel substrate; and

S2: immersing the gel substrate in a lubricating fluid to obtain an amphiphilic siloxane gel.

Further, in S1, the mixing is stirring and mixing well at 60-100°C at a stirring rate of 200-1000 r/min, and the ring-opening polymerization is reacting under nitrogen or an inert gas condition at 40-200°C for 3-40h, and then reducing the temperature to room temperature.

Further, in S2, the immersing time of gel substrate is carried out a temperature ranging from 25 °C to 50 °C for a time period ranging from 6h to 36h.

In S1, if the mixing effect of the active species and the cyclic siloxane is not good, it can be assisted by the addition of silicone oil or an organic solvent, wherein the organic solvent can be one of toluene, n-hexane, acetone and tetrahydrofuran.

The present application also provides use of the amphiphilic siloxane gel described above, which is used for preparing an anti-fouling coating.

The technical solution of the present application has the following advantages:

(1) In the present application, organic bases with specific groups is used as active species, and the active species has multiple roles in the preparation of gels: firstly, as a

catalyst for the polymerization reaction, it catalyzes ring-opening polymerization reaction of cyclic siloxanes to synthesize the gel substrate; secondly, it can be used as a static interaction aggregation unit to form a micro-phase separation structure, and the active species serves as the main body that constitutes the micro-phase of the hydrogel, and in the gel material ultimately obtained, the charging function and hydrogen-bonding function of the phase acts synergistically to realize physical cross-linking of the material and toughening it, so as to make the material have high toughness and high elasticity mechanical properties; finally, the active species also acts as an active catalyst, so as to enable the molecular bonds forming the gel substrate to have dynamically reversible breaking/generating properties, thus offering the gel with degradability/self-polishing properties.

(2) In the material of the present application, the active species has hydrophilicity and the siloxane has hydrophobicity, and the prepared gel, when used as a coating, has a hyper-slippery effect on both water and oil systems.

(3) In this application, a lubricant is introduced into the gel, and as the surface lubricant is depleted during use, the lubricant within the gel material is continuously emerged and replenished to the surface to maintain lubrication.

(4) The active species catalyst in the present application is a typical cationic group, and the introduction of this cationic group results in a final amphiphilic hyper-slippery gel that combines excellent antimicrobial properties.

(5) The amphiphilic siloxane gel described in the present application can also be gradually degraded to polydimethylsiloxane and the alkyl compounds corresponding to the active species catalyst under the catalysis of its own active species. Its degradation condition is an open system, and the degradation speed is accelerated with the increase of temperature; and the gel can also realize the reversible dynamic exchange of silicon-oxygen bond under the catalysis of its own active species, and help it to change from a non-linear crosslinked network with high internal stress to a linear non-crosslinked network with low internal stress, so as to better realize the purpose of degradation.

(6) The amphiphilic siloxane gel obtained by the present application has self-polishing and anti-fouling properties when used as a coating, and with the loss of lubricating fluid in the gel, resulting in less or no lubricating fluid being emerged in the material, the active

species present in the gel phase of the material will catalyze the degradation of the material, replenish the lubricating fluid to achieve continuous emerging, and ultimately achieve the degradation of the whole amphiphilic siloxane gel coating; at the same time, the chemical balance of catalytic degradation of the active species can be controlled by selecting the appropriate active species content and the swelling degree of the lubricating fluid to achieve the coating self-polishing rate control while meeting the demand for mechanical properties in the application of anti-fouling coatings.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to more clearly illustrate the specific embodiments of the present application or the technical solutions of the prior art, the accompanying drawings to be used in the detailed description or the prior art will be briefly introduced below, and it will be obvious that the accompanying drawings in the following description are some of the embodiments of the present application, and that other accompanying drawings may be obtained in accordance with these drawings without creative labor for a person of ordinary skill in the art.

FIG. 1 is a nuclear magnetic spectrum of the gel substrate obtained in Example 1 of the present application;

FIG. 2 is a practicality picture of the gel obtained in Example 1 of the present application;

FIG. 3 is a schematic diagram of the dynamic network structure of the amphiphilic siloxane gel obtained in Example 1 of the present application;

FIG. 4 is a compressive stress-strain curve of the gel substrate obtained in Example 1 of the present application;

FIG. 5 is a morphological diagram of a droplet on the surface of the amphiphilic siloxane gel obtained in Example 1 of the present application;

FIG. 6 is a diagram of the antimicrobial effect experiment in Test Example 3 of the present application;

FIG. 7 is a diagram of the anti-fouling effect experiment in Test Example 3 of the

present application;

FIG. 8 is a graph of the effect of the active species content on the release amount when the swelling degree of the lubricating liquid is 100 wt% of the substrate in Test Example 4 of the present application;

FIG. 9 is a graph of the effect of the swelling degree of the lubricating liquid on the release amount when the active species content is 10 wt% of cyclic siloxane monomer in Test Example 4 of the present application; and

FIG. 10 is a diagram comparing the viscosity of the gel material obtained in Example 1 and Comparative Example 1 in a complex situation in Test Example 5 of the present application.

DETAILED DESCRIPTION OF THE INVENTION

Example 1

This example provides an amphiphilic siloxane gel, which was prepared specifically as follows:

(1) 0.5 g of tetramethylammonium silanol was added into 10 g of octamethylcyclotetrasiloxane, stirred and mixed well at 80° C, and then placed in a nitrogen atmosphere at 85° C to react for 12 h. After the reaction was completed, it was placed in an open environment at room temperature, and cooled to room temperature, then the gel substrate could be obtained. Its NMR diagram is shown in FIG. 1, which shows obvious peak of methyl group linked to silicon at 0 ppm and obvious peak of methyl group linked to nitrogen at 3.25 ppm.

(2) The obtained gel substrate was immersed in 50 cst dimethyl silicone oil until it reached equilibrium, and the amphiphilic siloxane gel was obtained. The practicality picture of the material is shown in FIG. 2, and it can be seen that it is a semi-transparent elastomer, and its structure is shown in FIG. 3, which is a dynamic network.

Example 2

This example provides an amphiphilic siloxane gel, which was prepared specifically as follows:

(1) 0.5 g of tetrabutylphosphine hydroxide was added into 20 g of

decamethylcyclopentasiloxane, stirred and mixed well at 60° C, and then placed in a nitrogen atmosphere at 100° C to react for 12 h. After the reaction was completed, it was placed in an open environment at room temperature, and cooled to room temperature, then the gel substrate could be obtained.

(2) The obtained gel substrate was immersed in 20 cst dimethyl silicone oil until it reached equilibrium, and the amphiphilic siloxane gel was obtained.

Example 3

This example provides an amphiphilic siloxane gel, which was prepared specifically as follows:

(1) 0.5 g of tetrabutylammonium hydroxide was added into 30 g of dodecamethylcyclohexasiloxane, stirred and mixed well at 90° C, and then placed in a nitrogen atmosphere at 60° C to react for 20 h. After the reaction was completed, it was placed in an open environment at room temperature, and cooled to room temperature, then the gel substrate could be obtained.

(2) The obtained active gel substrate was immersed in 1000 cst dimethyl silicone oil until it reached equilibrium, and the amphiphilic siloxane gel was obtained.

Comparative Example 1

A conventional siloxane gel was provided in this comparative example, and the difference between this comparative example and Example 1 was that a chemically crosslinked silicone elastomer was prepared by using a platinum catalyst to catalyze the addition reaction and curing, and the elastomer obtained was swollen with a silicone oil with a viscosity of 1000 cst, so as to prepare and obtain an inactive, non-amphiphilic silicone gel.

Comparative Example 2

This comparative example provided a conventional anti-fouling coating, which was Hempaguard X7 89900, an organosilicon anti-fouling paint manufactured by HEMPEL company.

Test Example 1

The compressive stress-strain curve of the gel substrate obtained in Example 1 was measured in an instron-9347 model universal materials testing machine from Instron company, as shown in FIG. 4. As can be seen from the figure, no obvious change in the

compressive stress-strain curve was observed in 10,000 cycle tests, indicating that the material has excellent mechanical properties.

Test Example 2

The amphiphilic siloxane gel obtained in Example 1 was made into a coating. Its hyper-slippery effect is shown in FIG. 5. It can be seen that compared with the surface of the material without silicone oil, a droplet can roll to the edge within 30 s on the surface of the hyper-slippery gel coating of the active amphiphilic hyper-slippery gel, whereas it only shows a very short rolling distance on the surface of the material without silicone oil.

Test Example 3

The amphiphilic siloxane gel obtained in Example 1 was made into a coating, which was compared with a blank metal surface, as well as with a conventional anti-fouling coating in Comparative Example 2 for antimicrobial performance test and anti-algae adhesion test, with comparative effects as shown in FIGS. 6 and 7, respectively. The amphiphilic siloxane gel shows obvious antimicrobial effect, its inhibition rate is more than 90, and at the same time shows a lower rate of algae adsorption.

Antimicrobial Performance Test Method

E. coli (DH5α wild type) was incubated in 5 ml LB culture medium at 37°C for 12 h. It was added into Luria-Bertani (LB) culture medium with a concentration of about 10^9 CFU/ml, and 3 ml of bacterial suspension was added to immerse each sample. The three sets of experimental samples were incubated at room temperature for 24 h. After incubation, the samples were removed from the bacterial suspension. Each sample was gently washed three times with 1 ml of PBS. Then, the samples were stained with live/dead BacLight™ Bacterial Survival Kit (Thermo Fisher) for 15 min. The samples were then washed 3 times with PBS to remove excess dye and then observed under a fluorescence microscope.

Anti-Algae Adhesion Test Method

Three sets of samples, i.e., blank metal sheet, metal sheet coated with amphiphilic siloxane gel coating obtained in Example 1, and metal sheet coated with conventional anti-fouling coating in Comparative Example 2, were immersed in a generation of algae culture solution with a concentration of 1 g/L and placed in a incubator, and DMEM culture solution was added every 12 hours to make the algae grow, and the three sets of samples

were taken out after one week, and after slight washing in deionized water, photographs were taken, and the percentage of algae coverage on the surface of the samples was counted using the software image pro in the image size molecule.

Test Example 4

(1) The raw materials of Example 1 were used, the swelling degree of the lubricating liquid was 100 wt% of the substrate, and the active species content was adjusted to 5 wt%, 7.5 wt%, 10 wt%, and 15 wt% of the substrate, respectively, and the above materials were used to test the effect of the active species content on the mechanical properties and degradation/self-polishing properties. The results are shown in Table 1 and FIG. 8, in which the degradation/self-polishing properties are expressed by the release amount of lubricating liquid after the gel has been left to stand for a certain period of time:

Release amount = (initial weight of the gel - weight after erasing the lubricating liquid from the gel surface)/initial weight of the gel:

Table 1: Effect of active species content on mechanical properties

Active species content (%)	5	7.5	10	15
Modulus of elasticity (MPa)	1.2	1.32	1.78	2.84

As can be seen from the above table, the higher the active species content, the better the mechanical properties, and at the same time the lower the release amount as can be seen from FIG. 8.

(2) The raw materials of Example 1 were used, the active species content was 10 wt% of the substrate, and the swelling degree of the lubricating liquid was adjusted to 150 wt%, 100 wt%, 75 wt%, and 50 wt% of the substrate, respectively, to investigate the effect of the active species content on the mechanical properties and the degradation/self-polishing properties. The results are shown in Table 2 and FIG. 9, wherein the degradation/self-polishing properties are expressed by the release amount of lubricating liquid after the gel has been left to stand for a certain period of time:

Release amount = (initial weight of the gel - weight after erasing the lubricating liquid from the gel surface)/initial weight of the gel:

Table 2 Effect of swelling degree of the lubricating liquid on mechanical properties

Swelling degree of the	150	100	75	50

lubricating liquid (%)				
Modulus of elasticity (MPa)	0.74	0.96	1.2	1.6

From the above table, it can be seen that the lower the swelling degree of the lubricating liquid, the better the mechanical properties, and at the same time the lower the release amount as can be seen from FIG. 9.

It can be seen that by varying the swelling degree of the lubricating liquid and the content of the active species, the mechanical properties and the degradation/self-polishing properties can be adjusted so as to achieve the desired effect.

Test Example 5

The materials obtained in Example 1 and Comparative Example 1 were taken for comparison of viscosity in a complex situation. As shown in FIG. 10, three droplets of aqueous solution droplets (red) dispersed with surfactants (5% Tween 80 and 5% polyethylene glycol of molecular weight 2000) with sizes of about 5μl and 25μl respectively, and three droplets of ethanol solution droplets (blue) dispersed with surfactants with sizes of about 5μl and 25 μl respectively, were added dropwise on the samples coated with the materials of Example 1 (top left) and Comparative Example 1 (top right), respectively. The entire samples were placed on a table with an inclination angle of 10°, and the movement changes of the droplets on the surface of the coatings was observed.

As can be seen from FIG. 10, both kinds of droplets slid away from the surfaces of the samples of Example 1 without adhering. However, on the sample in Comparative Example 1, the small droplets all spread out directly and could not slide. After 60 seconds, both the blue droplets and the red droplets slid away from the samples in Example 1 (lower left) without adhering to the coating, and on the sample in Comparative Example 1 (lower right), both kinds of droplets spread out and adhered to the coating surface. That is, it is shown that the sample prepared in Example 1 of the present application can cope with more complex adhesion items than the conventional silicone gel in Comparative Example 1.

Obviously, the above embodiments are merely examples for the purpose of clear illustration and are not a limitation of the embodiments. For those skilled in the art, other variations or changes in different forms may be made on the basis of the above description. It is neither necessary nor possible to exhaust all of the embodiments herein. The obvious

variations or changes derived therefrom remain within the scope of protection of the present invention.