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SHORT COMMUNICATIONS

A Novel Method of Dissolving Chitosan in Water for Industrial Application

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Chitosan has been recently focused attention because it is one of naturallyoccurring, biodegradable polymer[1] and shows various pharmacological activities such as anti-fungal,[2,3] anti-allergic,[4] anti-tumor,[5] immune-activating[6,7] effects and so on. Therefore, it was expected to use chitosan as medical materials as well as chitin. Some chitosan-containing textiles were developed and were already used for commercial cloths expecting its anti-fungal activity. In these cases, however, powdery chitosan were mixed with substrate polymer and, therefore, heterogeneous material is formed. Chitosan does not dissolve in water and in usual organic solvents except for some specific one containing fluorine, so it is difficult to mix it microscopically with other polymers using solvents.

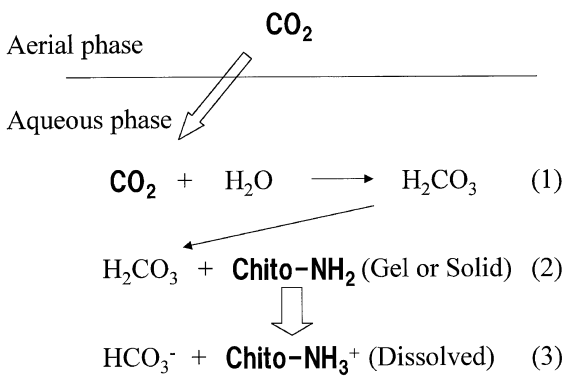
Chitosan, however, dissolves in various aqueous solutions containing organic and inorganic acids because it is only basic polymer occurring naturally. It is possible to use these chitosan solutions for preparing films or fibers by evaporating the water. However, these films or fibers still contains acids, so they are soluble in water. This property is not desirable from the view point of textile production, so the treatment with alkali solution to eliminate acids from the surface of the products is required but it is troublesome and requires time and money because a large plant might be necessary for this purpose. In addition, such treatment damages the surface coated with chitosan. On the other hand, when chitosan solution is used as medicals, existence of acid lowers pH and has a bad influence on skin.

A substance, which acts as an acid for dissolving chitosan in water and is naturally removed in the process of preparing films or fibers as well as it does not lower pH of the solution, must be very useful from industrial point of view. We reached to an idea to use carbonic acid gas (CO_2 gas) as such material.

RESULTS AND DISCUSSION

The Process of Dissolving Chitosan

Scheme 1 shows the role of CO_2 gas for dissolving chitosan in water. First, chitosan is emulsified in water then CO_2 gas is bubbled in it. CO_2 gas dissolves in water (the solubility is 0.82 mL/mL H_2O, 25°C, 1 atm) and CO_2 molecule reacts with H_2O molecule forming H_2CO_3 (eq 1). This reaction stops in a equilibrium state, which inclines extremely to the left-hand side ($[H_2CO_3]/[CO_2] = 0.0037$). Carbonic acid, H_2CO_3, is a weak acid and the pK_{a1} is acknowledged to be 6.4.[8]



Scheme 1.

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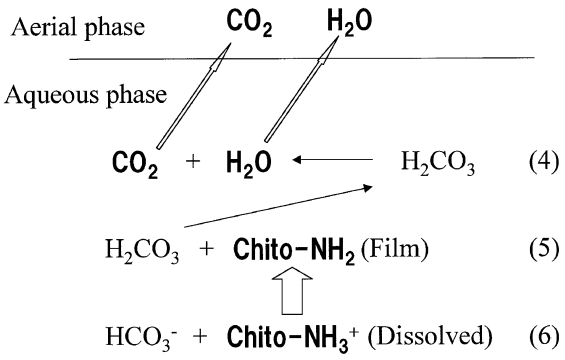

Scheme 2.

However, this is the value calculated assuming that all the CO_2 molecules dissolved changes into H_2CO_3. Therefore, real pK_{a_1} value for the reaction, H_2CO_3 = H^++ $HCO3^-$, becomes 3.9 when calculated using above equilibrium constant.[9] This means that H_2CO_3 is an acid stronger than acetic acid (pK_a = 4.6) and near lactic acid (pK_a = 3.7). As well-known, aqueous acetic acid solution has the ability to dissolve chitosan and lactic acid also has the ability stronger than acetic acid, so CO_2 gas, namely H_2CO_3., seems also to have the ability. Chitosan has a amino group and, therefore, is a base and reacts with the carbonic acid (eq 2) forming a cation (eq 3). This chitosan cation is water soluble. That is to say, chitosan is dissolved into water by carbonic acid gas. By this reaction, H_2CO_3 is consumed and reaction 1 moves toward the right-hand side. This means the solubility of CO_2 gas is increased by chitosan.

The Process of Forming Chitosan Film From the Chitosan Solution

Scheme 2 shows the process in which chitosan film is formed from the above-mentioned chitosan solution. During the evaporation of water, the CO_2 molecules dissolved in water also evaporates easily. For compensating the loss of them, H_2CO_3 is decomposed according eq 4. This reaction induces the change of the dissolved chitosan into a solid film (eqs 5 and 6). After finishing evaporation or drying the solution, chitosan film is formed and no acid is remained.

Dissolving of Deacetylated Chitin (DAC 50)

The chitin, 50% of which acetamido group is hydrolyzed randomly, is called DAC 50. This substance is a kind of chitosan and is known to be water-soluble in contrast to the cases of chitin and chitosan. However, if DAC 50 is solidified by evaporation of water, it becomes impossible to dissolve it in water again without adding any acid. We tried to dissolve this DAC 50 by using CO_2 gas. Solid DAC 50 (Koyo Chemicals Co., Ltd.) was first dispersed in water (Figure 1, A), then,

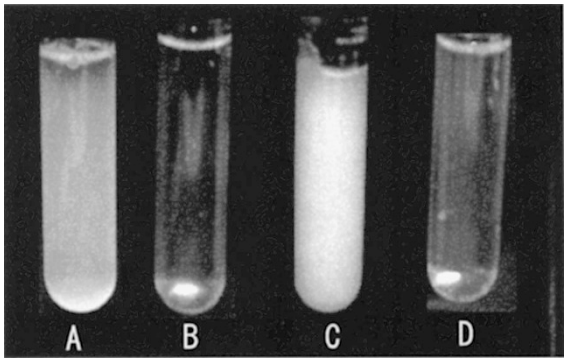

Figure 1. Photographs of DAC 50 dispersed in water (A) and after bubbling CO_2 gas (B), chitosan gel dispersed in water (C) and after bubbling CO_2 gas (D).

CO_2 gas was bubbled in it. For about a few ten seconds, the solution became transparent as shown in Figure 1, B and the viscosity of the solution abruptly increased. This results means that DAC 50 was dissolved perfectly with CO_2 gas.

Dissolving of Chitosan Gel

Chitosan gel is formed by dissolving chitosan with HCl then neutralized the solution by adding NaOH solution. Chitosan gel was prepared from powdery chitosan (chitosanPSH, Yaizu Suisan Co., Ltd.) by this way, washed with water repeatedly and dispersed in water (Figure 1, C), then, CO_2 gas was bubbled in it. For about a few minute, the solution became transparent as shown in Figure 1, D and the viscosity of the solution abruptly increased, showing that chitosan gel was also dissolved perfectly with CO_2 gas.

Dissolving of Powdery Chitosan

We tried to dissolve powdery chitosan because chitosan is usually commercially- available as a powder. Powdery chitosan was dispersed in water and CO_2 gas was bubbled in it as the former cases. However, powdery chitosan did not disappear even for a few hour bubbling of CO_2, nevertheless the viscosity of the solution increased showing that a small fraction of chitosan was dissolved. We thought that concentrated CO_2 is necessary to dissolve powdery chitosan and tried to increase the solubility of CO_2 by applying high pressure CO_2. The solution in which powdery chitosan was dispersed was stirred with magnetic stirrer and CO_2 gas was dissolved at high pressure (5–6 atm) using a high pressure apparatus. However, it seemed to take more than two weeks for the perfect dissolving.

Formation of a Chitosan Film From the Solution

The solutions of both DAC 50 and chitosan gel were spread on a glass and dried spontaneously. In both cases, a thin film was left on a glass adhering strongly

on it.

From above results and discussion, it was shown that chitosan is easily dissolved with CO_2 gas by way of the formation of chitosan gel. Preparation of chitosan gel is industrially not so serious problem because it is prepared temporarily in the process of purification of chitosan. A film prepared from chitosan gel did not dissolve in water in contrast to the cases using various acid solutions. Therefore, we think this solution will open up a new way to coat various membranes and fibers with thin chitosan film in order to confer pharmacological functions to them. The pH values of both solutions prepared from DAC 50 and chitosan were neutral (6.8) in contrast to the case using acids. This develops potential of this chitosan solution in medical industry and seems to be superior to the reported ways.[10] We are now planning to coat cellulose-derived materials with this solution.

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