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Selective permeabilities of chitosan-acetic acid complex membrane and chitosan-polymer complex membranes for Oxygen and Carbon dioxide

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Summary

Chitosan-acetic acid complex membrane and several chitosan-polymer complex membranes have been prepared and the gas permeabilities of these membranes have been examined. It has been found that chitosan-acetic acid complex membrane shows high permselectivities for oxygen and carbon dioxide, and synthetic polymers can modify the permeation behavior of chitosan membrane for oxygen and carbon dioxide. The separation factor α_{CO_2/O_2} of these membranes were much smaller than unity, indicating possible applications for the preservations of fruits and vegetables. It has been noticed that the permeation behaviors of these membranes are markedly influenced by metal ions added into the membranes and the membranes have good mechanical strength.

Introduction

Recently, a great deal of attentions have been paid to the applications of polymer membranes to the preservations of fruits and vegetables, because the selective permeabilities of polymer membranes for gases can be utilized to control atmosphere to retard fruit and vegetable respiration. There are a number of papers published (1-5).

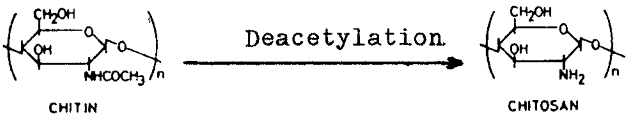
It has been known that the separation factor for gas permeation of membrane can be expressed as

$$\alpha_{a/b} = P_a/P_b$$

P —— permeability coeffecient, a,b —— different gases.

We have observed $\alpha_{CO_2/O_2} > 1$ for general polymer membranes, but Yun et al. (6,7) found $\alpha_{CO_2/O_2} < 1$ for the membranes of hydrogen-bonded polymer complexes and reported that these membranes are more effective for the preservations of fruits and vegetables than the other polymer membranes reported in literatures.

Chitosan is a natural polymer and it can be produced from chitin which is usually obtained from crab or shrimp shells. We have utilized chitosan containing hydroxyl groups and amino groups to prepare chitosan-acetic acid complex membrane and several chitosan-polymer hydrogen-bonded complex membranes,



and found that these membranes have much lower permeabilities for carbon dioxide than for oxygen. This interesting property of the membranes are just desirable for preservations of fruits and vegetables. We have also noticed that the membranes have good mechanical properties.

Results and Discussion

Mechanical strength is very important for applications of polymer membranes. Table 1 shows the mechanical properties of chitosan-acetic acid complex membrane and chitosan-polymer complex membranes. We can see that these membranes possess higher tensile strengthes, and in addition, the tensile strength and tensile modulus of the membranes are enhanced with addition of the metal ions. This is attributed to the crosslinking between polymer chains by metal ions. Good mechanical properties of chitosan make it possible to use as a polymer membrane material.

The results in Table 2 show that the separation factor α_{CO_2/O_2} of chitosan-acetic acid complex membrane is 0.075, which is smaller than that of chitosan membrane (8), 0.75 and that of hydrogen-bonded polymer complex membrane, polyacrylic acid-polyvinyl alcohol, 0.16 (6,7), and which is much smaller than unity. The unusual permeation behavior of chitosan-acetic acid complex membrane for oxygen and carbon dioxide indicates its possible applications in fruit and vegetable preservation. In fruit and vegetable atmosphere-controlled preservations, it is necessary to keep the fruits and vegetables under an atmosphere of high carbon dioxide and low oxygen content to slow down the metabolic process of fruits and vegetables. The low permeability of carbon dioxide through the chitosan-acetic acid complex membrane can prevent carbon dioxide evolved in the respiration process of fruits and vegetables from escaping, so it is possible to make an atmosphere containing a higher content of carbon dioxide.

Table 1 Mechanical properties of the membranes

Membrane	Tensile strength (kg/cm^2)	Elongation at break (%)	Tensile modulus (kg/cm^2)$\times 10^4$
CS-AcOH	639	10	4.73
CS-Ni(II)*	1004	16	5.86
CS-Cu(II)	753	11	4.89
CS-PEG	453	38	2.00
CS-PEG-Ni(II)	515	7	2.72

CS: chitosan; AcOH: acetic acid; PEG: polyethylene glycol.
* The mole ratio of metal ion to $-NH_2$ of chitosan is 0.1.

Table 2 Permeation behaviors of chitosan-acetic acid complex membrane and chitosan-polymer complex membranes

Membrane	P_{O_2}(barrers)^a	P_{CO_2}(barrers)	α_{CO_2/O_2}
CS-AcOH	0.943	0.0703	0.075
CS	-	-	0.75
PAA-PVA	0.90	0.143	0.16
CS-PVA^b	4.04	1.01	0.26
CS-PEG	1.58	0.558	0.35
CS-PAm	1.59	0.118	0.074
CS-PVP	1.60	0.818	0.51

PVA: polyvinyl alcohol; PAm: polyacrylamide; PVP: polyvinylpyrrolidone

a) barrers: 10^{-10} cm^3(STP)-cm/cm^2-sec-cmHg.

b) amino group of chitosan/repeating unit of polymer = 1 (mole)

No single combination ratio of carbon dioxide to oxygen is best for the preservation of various kinds of fruits and vegetables. It has been recognized that different fruits and vegetables must be preserved under an atmosphere with different ratios of carbon dioxide to oxygen by studying fruit and vegetable atmosphere-controlled preservations (9), so the polymer membranes having different α_{CO_2/O_2} are required for preservations of fruits and vegetables. Miya et al. (10) found the hydrogen bond interactions between OH of polyvinyl alcohol and OH or NH_2 of chitosan occur by Fourier-transform infrared spectroscopy, so hydrogen-bonded complex polymer can be formed from chitosan and polyvinyl alcohol. We have prepared several membranes utilizing chitosan and water-soluble polymers which contain functional groups to form hydrogen bonds with OH or NH_2 of chitosan, and examined the permeabilities of the membranes for carbon dioxide and oxygen (Table 2). It have been noted that in comparison with that of chitosan-acetic acid complex membrane P_{O_2} and P_{CO_2} of chitosan-polymer complex membranes increase, and α_{CO_2/O_2} of chitosan-polymer complex membranes are different from that of chitosan-acetic acid complex membrane except that of chitosan-polyacrylamide membrane. These results provide more convenience for selecting suitable preservation membranes of fruits and vegetables.

Chitosan containing amino groups is a natural chelating polymer and a great number of chitosan-metal complexes have been reported (8,11,12). We have also investigated the effects of metal ions on the permeation behavior of chitosan-acetic acid complex membrane and chitosan-polymer complex membranes. The results are summarized in Tables 3, 4 and 5. We can see that P_{O_2} increases for chitosan-acetic acid complex membrane with addition of metal ions, and it has a little change for chitosan-polyethylene glycol membrane, but P_{CO_2} either for

Table 3 Effects of metal ions on the permeability of chitosan-acetic acid complex membrane

Metal ion	P_{O_2}(barrers)	P_{CO_2}(barrers)	α_{CO_2/O_2}
—	0.943	0.0703	0.075
Ni(II)	1.80	0.0532	0.030
Mn(II)	1.68	0.0543	0.032
Co(II)	1.55	0.0711	0.046
Cu(II)	1.23	0.0610	0.050

The mole ratio of metal ion to amino group of chitosan is 0.1.

Table 4 Influence of metal ions on the permeability of chitosan-polyethylene glycol membrane

Metal ion	P_{O_2}(barrers)	P_{CO_2}(barrers)	α_{CO_2/O_2}
—	1.58	0.558	0.35
Ni(II)	1.70	0.0852	0.050
Mn(II)	1.92	0.168	0.087
Co(II)	1.37	0.0926	0.068
Cu(II)	1.34	0.0511	0.038

Amino group of chitosan : repeating unit of PEG : metal ion = 1 : 1 : 0.1 (mole).

Table 5 Summary of effects of metal ions on the separation factors of the membranes for carbon dioxide and oxygen

Membrane	Separation factor α_{CO_2/O_2}				
	—	Ni(II)	Mn(II)	Co(II)	Cu(II)
CS-AcOH	0.075	0.032	0.046	0.030	0.050
CS-PEG	0.35	0.050	0.087	0.068	0.038
CS-PAm	0.074	0.021	0.065	0.029	0.057
CS-PVP	0.51	0.049	0.055	0.085	0.068
CS-PVA	0.26	0.032	0.028	0.066	—

Amino group of chitosan : repeating unit of polymer : metal ion = 1 : 1 : 0.1 (mole).

chitosan-acetic acid complex membrane or for chitosan-polyethylene glycol membrane almost all decreases when metal ions are added. We can also observe that the effects of metal ions on α_{CO_2/O_2} of either chitosan-acetic acid complex membrane or chitosan-polymer complex membrane are evident. The α_{CO_2/O_2} of the membranes decrease markedly with addition of metal ions. Ni(II) is more effective than the other metal ions in most of these membranes. The results may be due to two reasons. First, the membrane micro-structures are altered when coordinating groups of polymer complex with metal ions, so permeabilities of carbon dioxide and oxygen are changed. Second, the complex of metal ions with carbon dioxide reduces the permeation rate of carbon dioxide through the membranes.

Experimental

Materials

Polymers were synthesized in general methods. Polyvinyl alcohol and polyethylene glycol are commercial reagents. Polyvinyl alcohol has degree of polymerization, 1700 and degree of hydrolyzation, 88%. Molecular weight of polyethylene glycol is 20,000. Commercial chitosan with 82% of deacetylation degree was used.

Preparation of membrane

Chitosan-acetic acid complex membrane was formed by casting an aqueous solution of 0.86% chitosan containing 1.3% acetic acid on a glass plate. The chitosan-polymer complex membranes were obtained by mixing a chitosan solution and a polymer solution, and then casting the mixture of the solution on a glass plate.

Preparation of membranes containing metal ions

An aqueous solution of metal chloride was added into a solution of chitosan and stirred. After about 30 minutes, the mixed solution was casted on a glass plate. A membrane containing metal ions was obtained after the solvent evaporated at room temperature.

Measurement of gas permeability

Permeabilities of the membranes for oxygen and carbon dioxide were measured by gas chromatography. The measurements were carried out at 0.8 kg/cm^2 driving pressure and ca. 25^oC. Thickness of the membranes is 20-30 µm. The membrane area in contact with the gas is 19.6 cm^2.

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