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Cellular structure in an *N*-acetyl-chitosan membrane regulate water permeability

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ABSTRACT

A novel model of the water permeation mechanism in an *N*-acetyl-chitosan membrane with a cellular structure is proposed. Although the entire membrane structure has a hydrophilic character, the cellular structure incorporates junction zones that practically prevent water permeation. Chitosan membranes with a controlled degree of deacetylation (DD) were prepared using a casting method. Changes in the water flux and total water content of the membrane were observed with a change in DD. The membrane properties were analyzed and evaluated using water permeability measurements, scanning electron microscopy (SEM), X-ray diffraction (XRD), and differential scanning calorimetry (DSC). SEM observations indicated that the membrane structure was an individual cellular structure and that this cellular structure grew with decreasing DD. XRD measurements indicated the crystal structure of the membrane was amorphous regardless of the DD in the experimental range. The free water content (W_f), the freezable bound water (W_{fb}), and the bound water not able to freeze (W_b) were evaluated by DSC. The free water mainly contained inside the cellular structure, and resulted in swelling the chitosan membrane. Water flux was measured using ultrafiltration apparatus; it was dependent on the operational pressure, membrane thickness, and the feed solution viscosity, and obeyed the Hagen–Poiseuille flow. At a higher DD, water permeation proceeds due to degradation of the cellular structure; the amount of water in permeation channels was greater than that for lower DD membranes even though the total water content in the membrane was less. The water flux of the chitosan membrane was determined by the water content constructing channels through the membrane and not on the total water content in the membrane.

1. Introduction

Membrane fouling, especially "biofouling" [1], negatively influences the permeation flux and the performance of some membrane properties (e.g., reduced salt rejection and elevated operational pressure) [2–5]. Chitosan is known as a biopolymer material (Fig. 1) that inhibits the growth of mold and bacteria [6], and is expected to provide long-life hygienic membrane processing.

Control of water flux is very important for separation processes using a chitosan membrane. Therefore, a detailed investigation of the influence of the structure and water content of the membrane on the water flux is necessary for desirable control of water permeation.

The degree of deacetylation (DD) of a chitosan membrane is stoichiometrically controlled to a designed level based on the observed linear relationship between the DD and the amount of acetic anhydride additive. Although a chitosan membrane produced under lower DD conditions has more hydrophilic character and becomes apparently swollen with water, the permeated water flux through such membranes is dramatically reduced [7]. This observed trend did not agree with the general known behavior of hydrophilic membranes.

This paper demonstrates the preparation of a chitosan membrane by a casting method in combination with *N*-acetylation to control molecular properties (i.e., DD). The effects of the DD of chitosan on permeability and hydrophilic character are discussed and a novel model of the water permeation mechanism in an *N*-acetyl-chitosan membrane with a cellular structure is proposed.

2. Materials and methods

2.1. Preparation of an N-acetyl-chitosan membrane

6 g of chitosan (low molecular weight, Sigma–Aldrich) and 3 g of polyethylene glycol (MW: 7500, Wako) were dissolved in 111 g of 10 (v/v)% acetic acid. The chitosan solution was diluted to 2

Abbreviations: CPS, counts per second; DD, deacetylation degree; DSC, differential scanning calorimetry; MW, molecular weight; SEM, scanning electron microscope; XRD, X-ray diffraction.

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Nomenclature

A	additive volume of acetic anhydride (μl (50 g chitosan solution of 2 wt%)$^{-1}$)
A_m	apparent surface area of the membrane (m^2)
A_p	total cross-sectional area of pore of the membrane (m^2)
DD	deacetylation degree (%) previously defined in our paper [7]
D_p	diameter of pore in membrane (m)
J_v	volumetric water flux ($m^3\ m^{-2}\ s^{-1}$)
L_m	thickness of membrane (m)
L_p	length of pore membrane (m)
n	total number of pore
N_p	numerical density of pores (m^{-2})
Q_{endo}	endothermic heat per unit mass of swollen membrane (J (g of w_e)$^{-1}$)
Q_f	heat of fusion of ice; (333.9 J (g of water)$^{-1}$)
R_t	volumetric ratio of total contained water of membrane
R_1	volumetric ratio of contained water in the channels
R_2	volumetric ratio of immobilized water content inside cells
u	flow rate of water in pore D_p (m s^{-1})
w_b	mass of bound water (g)
w_d	mass of dried membrane (g)
w_e	mass of swollen membrane at equilibrium ($= w_t + w_d$) (g)
w_f	mass of free water (g)
w_{fb}	mass of freezable bound water (g)
w_t	total mass of contained water in membrane ($= w_f + w_{fb} + w_b$) (g)
W_b	bound water content ratio defined as $w_b w_d^{-1}$ (g g^{-1})
W_f	free water content ratio defined as $w_f w_d^{-1}$ (g g^{-1})
W_{fb}	freezable bound water content ratio defined as $w_{fb} w_d^{-1}$ (g g^{-1})
W_t	total water content ratio defined as $w_t w_d^{-1}$ ($= W_f + W_{fb} + W_b$) (g g^{-1})

Greek symbols

ΔP	operational pressure (Pa)
θ	angle of X-ray diffraction (degree)
μ_L	viscosity of feed solution (Pa s)

(w/w)% with methanol and then vacuum-filtered. Desired amount of acetic anhydride (97.0 wt%, Wako) was added to the chitosan solution after vacuum filtration. A desired amount of cast solution (5–15 g) was introduced into a petri dish with a diameter of 75 mm and then dried for 12 h at 333 K, and subsequently gelled by immersion into a sufficient amount of 4% NaOH solution. The resultant membrane was washed with distilled water,

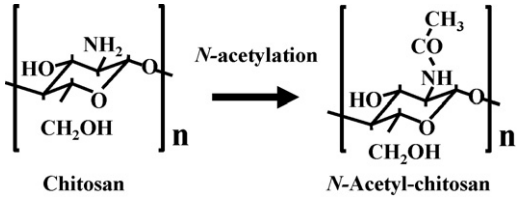

Fig. 1. Chemical structure of chitosan and *N*-acetyl-chitosan. Chitosan with an added acetyl group as the acyl group becomes *N*-acetyl-chitosan, and exhibits properties approximately equal to those of chitin.

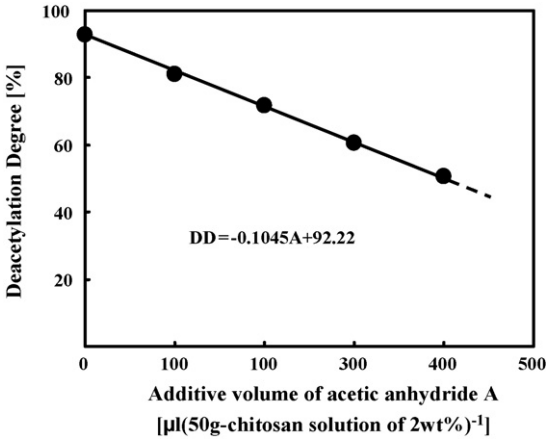

Fig. 2. Control of the DD in a chitosan membrane using a casting method in combination with *N*-acetylation (at 298 K). This figure was previously reported by the authors [7].

and a membrane was finally formed by placing it into hot water (353 K).

Colloidal titration is a method for measuring free amino groups in a chitosan solution, and the DD indicates molar percentages of glucosamine to the sum of glucosamine and acetylglucosamine. The DD of the chitosan membranes produced above were analyzed using the colloidal titration method, with potassium polyvinyl sulfate solution (2.5×10^{-3} N) as the titrant and toluidine blue as the indicator. The terminal point of titration was clearly confirmed by the change of color from blue to claret.

The relationship between the quantity of acetic anhydride (A) used in the preparation and the DD percentage of resultant chitosan (Fig. 2) [7] is given by

$$DD = -0.1045A + 92.22 \quad (1)$$

In the preparation of a membrane by the casting method, a DD range of over 50% is preferable to avoid solution gelation, even if the relationship is effective over the range of 0–100%. *N*-Acetyl-chitosans of DD 71.3%, 76.5%, 81.8%, 87.0%, and 92.2% were prepared for analysis.

2.2. Scanning electron microscopy (SEM)

The morphology of the chitosan membranes was observed using a scanning electron microscope (S-3500N, Hitachi High-Technologies Corporation, Tokyo) operated at an accelerating voltage of 10 kV. As a pretreatment for clear observation of the inner structure, the chitosan membrane was vacuum freeze-dried. The dried membrane samples were then coated with zinc.

2.3. X-ray diffraction

X-ray diffraction (XRD) patterns were recorded on a Rigaku RAD-C diffractometer (monochromatic Cu Kα radiation) with the X-ray cathode operated at 20 mA and 30 kV. The samples were supported on a glass frame and were determined at 2θ angles from 10° to 50°.

2.4. Water content

The total mass of water contained in the membrane (w_t) was defined to be the sum of three categories of water – free water (w_f), freezable bound water (w_{fb}), and bound water not able to freeze (w_b) – as shown in the following equation:

$$w_t = w_f + w_{fb} + w_b \quad (2)$$