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Electric resistance of chitosan derivatives

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Abstract

Direct compression of partially deacetylated chitin (DAC) and its derivatives gave tablets, which were found to be very convenient for the simple and swift estimation of the specific resistance under the various temperature and moisture conditions. The specific resistance (ρ) value of the 86% deacetylated chitin (DAC-86) tablet decreased with increasing the water content and temperature. The presence of metal chloride in the DAC-86 acetate tablet decreased the ρ value. The utilization of polyionic DAC derivatives such as *N*-carboxymethylated DAC-86, *N*,*O*-sulfated DAC-95, and *O*-methyl-*N*-trimethylated DAC-86 chloride gave improved ρ values (ca. 10^6–10^7 Ω cm at 20°C and RH = 40%) without the addition of acidic dopant and inorganic salts that would be easily lost by dissolution in water. These chitosan derivatives might be regarded as polyelectrolytes, which partially showed ionic conductivity.

Keywords: Chitosan; Chitin; Specific resistance; Ionic substituent; Ionic carrier; Polyelectrolyte

1. Introduction

In general, static electricity is generated and accumulated by rubbing different materials. Electrostatically charged materials adsorb the dust which floats in air, and the stored static electricity which exceeds insulation resistance at the space is rapidly discharged. These phenomena often cause various troubles not only in our daily life but also in the accurate working of electronic instruments. Materials, which possess low electric resistance, are necessary in order to prevent troubles caused by electrostatic accumulation. Because chitosan, a β-(1 → 4)-linked natural polysaccharide composed of 2-amino-2-deoxy-β-D-glucopyranose (D-glucosamine: GlcN) residue, has gained increasing attention owing to biocompatiblity (Shigemasa and Minami, 1995; Morimoto et al., 1996; Saimoto et al., 1996) and cationic property which might be advantageous for electric conductivity, the study on electric property of chitosan derivatives would be useful to develop biocompatible antistatic material (Mita and Kischka, 1986; Muzzarelli et al., 1974). Chitosan was industrially provided by deacetylation of chitin, a polysaccharide made up of β-(1 → 4)-linked 2-acetamido-2-deoxy-β-D-glucopyranose (*N*-acetylglucosamine: GlcNAc) units, which is widely distributed in nature as a component of bacterial cell walls and exoskeletons of crustaceans and insects. Degree of deacetylation (DDA) of partially deacetylated chitin (DAC) and degree of *N*-acetylation (DA) of partially *N*-acetylated chitosan (PAC) can be controlled by the deacetylating and *N*-acetylating conditions, respectively (Hirano et al., 1976; Morimoto et al., 1996). Concerning electric properties of DAC, there were only a few studies, in which the addition of acetic acid and metal salts as dopant was necessarily to improve the electric conductivity of DACs (Mohamed et al., 1995; Subban et al., 1996; Subban and Arof, 1996), since chitosan film itself cannot be expected to possess high electric conductivity (Muzzarelli et al., 1974).

In this study, we planned to develop biocompatible antistatic materials using chitosan derivatives. If chitosan derivatives possess ionic substituents, their electric resistance would be considerably low without addition of metal salts. Herein we report that *N*-carboxymethylated, *N*,*O*-sulfated, and *N*-trimethylated chitosan derivatives showed reasonably low electric resistance in the absence of dopant. For the purpose of estimating simply and conveniently the electric resistance of various chitosan derivatives, we employed tablets made by direct compression of chitosan samples. Especially, chitosan, a hydrophilic natural polysaccharide, is known to have high affinity to natural fiber such as cotton and wool. Taking the utilization as antistatic material for the functional textile into consideration, we investigated the electric conductivity of chitosan tablets whose water content was controlled by the relative humidity.

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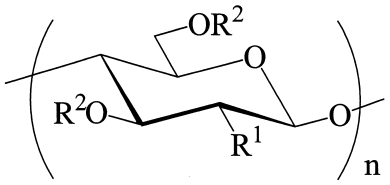

1. $R^1 = NH_2$, R^2 = H: chitosan
2. R^1 = NHAc, R^2 = H: chitin
3. $R^1 = NH_2$ or NHAc, R^2 = H: DAC, PAC
4. $R^1 = NH_2$, NHAc, or (NHMe, NHPr, or NHBu); R^2 = H: *N*-alkylated DAC
5. $R^1 = NH_2$ or NHAc; $R^2 = CH_2CH_2OH$ or H: *O*-2-HE-DAC
6. $R^1 = NH_2$, NHAc, or $NHCH_2COOH$; R^2 = H: *N*-CM-DAC
7. $R^1 = NH_2$, NHAc, or $NHSO_3H$; R^2 = H or SO_3H: *N,O*-sulfated DAC
8. $R^1 = NH_2$, NHAc, or $N^+Me_3\ Cl^-$; R^2 = H or Me: *O*-Me-*N*-TM-DAC

Fig. 1. Chitosan derivatives.

2. Experimental

2.1. Materials and installment

DAC-21 (Chitin EX, powder) and DAC-86 (Chitosan 10B, powder, number-average molecular weight (M_n) = 170 000) were purchased from Funakoshi Co. Ltd. and DAC-80 (Chitosan CLH, flake, M_n = 200 000) from Yaizu Suisankagaku Industry Co. Ltd. Unless otherwise noted, other reagents were purchased from Wako Pure Chem. Ind. Ltd. DDA and DA values were determined by the NMR and IR method (Shigemasa et al., 1996). Molecular weights of water soluble chitosan derivatives were determined by means of GPC (column: Asahipak GS-510H, GS-310M, GS-220H (7.6 × 250 mm); temperature: 50°C; carrier: 0.1 M AcOH/AcONa buffer (pH 4.8) containing 0.1 M NaCl or 0.67 M KH_2PO_4/Na_2HPO_4 buffer (pH 6.9), 1 ml min^{-1}; detector: RI; M_n: calculated on the basis of pullulan calibration). ^{1}H NMR spectra (270 MHz) were recorded on a JEOL JNM GX-270 spectrometer.

2.1.1. Preparation of chitosan derivatives (Fig. 1)

50% Partially *N*-acetylated chitosan (PAC-50) was prepared according to Hirano's method (Hirano et al., 1976), DAC-80 (Chitosan CLH, 2.0 g, 12 mmol as hexosamine residue) was dissolved in 2 wt% aqueous acetic acid (40 ml), and the resulting viscous solution was diluted with methanol (160 ml). A methanol (40 ml) solution of acetic anhydride (0.54 g, 5.3 mmol) was added to the DAC-80 solution in 30 min. After stirring for 4 h at room temperature, the reaction mixture was adjusted to pH 10 with 1 M NaOH. Washing of the precipitate formed with water and lyophilization gave PAC-50 as a colorless powder (1.6 g, 75% yield). When 0.1 M NaOH was added to a 0.1 wt% aqueous acetic acid solution containing PAC-50 (1 mg ml^{-1}), PAC-50 was soluble in the pH range 4–13. The DDA value was determined by the IR and ^{1}H NMR methods. IR (KBr) 1650, 1560, 1320 (amide), 1080 cm^{-1} (C–O–C); ^{1}H NMR (D_2O, one drop of 20% DCl): δ 2.06 (1.5 H, s, *N*-Ac), 3.1–4.1 (6 H, m, C2–C6 protons), 4.9–5.0 ppm (1 H, m, C1 proton); $M_n = 1.1 \times 10^5$.

Partial *N*-alkylation of 86% deacetylated chitin was prepared as follows. Reductive *N*-alkylation of DAC-86 with formaldehyde, propionaldehyde, or butyraldehyde was performed using Muzzarelli's method (Muzzarelli et al., 1983). An aqueous solution (20 ml) of the aldehyde (24 mmol, 2 equivalent relative to glucosamine residue) was added to DAC-86 (2.0 g, 12 mmol as glucosamine residue) dissolved in 2 wt% aqueous acetic acid (200 ml). After 30 min, $NaBH_4$ (0.50 g, 13 mmol) dissolved in water (50 ml) was added portion-wise to the reaction mixture for a period of 1 h at room temperature. The pH value of the reaction mixture was increased to 10 by adding 1 M NaOH, and the precipitate formed. The precipitate was washed with ethanol and water. Drying of the precipitate in vacuum at 60°C gave the *N*-alkylated derivatives as a colorless powder (1.9–2.4 g, 90%–95% yield). *N*-Methylated 86% deacetylated chitin (*N*-Me-DAC-86) (90% yield; degree of substitution (DS) = 0.5, calculated by the ^{1}H NMR analysis) showed IR (KBr) 2900 (CH), 1680 (C–N–C) 1650, 1320 (amide), 1080 cm^{-1} (C–O–C); ^{1}H NMR (D_2O, one drop of 20% DCl): δ 2.95 (1.6 H, s, N-CH_3), 2.06 (0.4 H, s, N-Ac), 3.1–3.9 (6 H, m, C2–C6 protons), and 4.9–5.0 ppm (1 H, m, C1 proton); $M_n = 10.0 \times 10^4$. *N*-Propylated 86% deacetylated chitin (*N*-Pr-DAC-86) (90% yield; DS = 0.7, calculated by the ^{1}H NMR analysis). IR (KBr) 2900, 2850 (CH), 1680 (C–N–C), 1650, 1320 (amide), 1080 cm^{-1} (C–O–C); ^{1}H NMR (D_2O, one drop of 20% DCl): δ 0.98 (2.1 H, t, J = 7.0 Hz, CH_3), 1.7–1.9 (1.4 H, m, CH_2), 2.06 (0.4 H, s, N-Ac), 3.1–4.0 (7.4 H, m, C2–C6 protons and N-CH_2), 4.9–5.0 ppm (1 H, m, C1 proton); $M_n = 9.1 \times 10^4$. *N*-Butylated 86% deacetylated chitin (*N*-Bu-DAC-86) (90% yield; DS = 0.8, calculated by the ^{1}H NMR analysis). IR (KBr) 2900, 2850 (CH), 1680 (C–N–C), 1650, 1320 (amide), 1080 cm^{-1} (C–O–C); ^{1}H NMR (D_2O, one drop of 20% DCl): δ 0.93 (2.6 H, t, J = 7.3 Hz, CH_3), 1.3–1.4 (1.7 H, m, CH_2), 1.7–1.8 (1.6 H, m, CH_2), 2.06 (0.4 H, s, *N*-Ac), 3.3–4.1 (7.7 H, m, C2–C6 protons and N-CH_2), 4.9–5.0 ppm (1 H, m, C1 proton); $M_n = 2.8 \times 10^4$.

N-Carboxymethylation of 86% deacetylated chitin was done according to Muzzarelli's method (Muzzarelli et al., 1982), an aqueous solution (20 ml) of glyoxylic acid (5.5 g, 5 equivalent relative to glucosamine residue) was added to DAC-86 (2.0 g, 12 mmol) dissolved in 2 wt% aqueous acetic acid (200 ml). After 30 min, $NaBH_3CN$ (0.50 g, 8.0 mmol) dissolved in water (50 ml) was added portion-wise to the reaction mixture for a period of 1 h at room temperature. The pH value of the reaction mixture was adjusted to 10 with 1 M NaOH. After addition of methanol (300 ml), the precipitate produced was centrifuged, washed

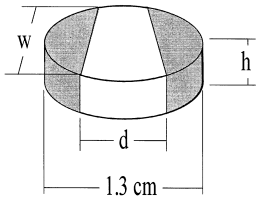

Fig. 2. Chitosan tablet for measuring electric resistance. ▤ Electrode of silver paste; *d*: electrode distance, 0.5 cm; *h*: thickness of tablet (cm); *w*: width of electrode, 1.1 cm.

with ethanol, and dissolved in water. Lyophilization of this solution gave *N*-carboxmethylated DAC-86 sodium salt (*N*-CM-DAC-86 (Na^+)) as a colorless powder (2.2 g, 90% yield; DS = 0.4, determined by the ^1H NMR analysis). IR (KBr) 3500–3400 (NH_2, OH), 2900, 2850 (CH), 1700 (C=O), 1650, 1320 (amide), 1080 cm^{-1} (C–O–C); ^1H NMR (D_2O): δ 2.07 (0.4 H, s, N-Ac), 2.5–2.6 (0.8 H, m, C2 proton), 3.3–3.9 (6.8 H, m, C2–C6 protons and N-CH_2CO), 4.5–4.8 ppm (1 H, m, C1 proton); $M_n = 34.0 \times 10^4$.

Sulfation of 86% deacetylated chitin was done by the modification of Wolfrom's method (Wolfrom and Han, 1959), DAC-86 (2.0 g, 12 mmol as glucosamine residue) was dissolved in 2 wt% aqueous acetic acid (200 ml), precipitated by the addition with 1 M NaOH, and washed with methanol, acetone, ether, and pyridine. Chlorosulfonic acid (5.0 ml, 64 mmol) was slowly added to the DAC-86 suspension in pyridine (20 ml). The reaction mixture was stirred at 100°C for 1 h, and cooled to room temperature. After addition of 2.5 M NaOH (30 ml) and ethanol (200 ml), the precipitate was washed with ethanol, redissolved in water, and dialyzed. Lyophilization of the aqueous solution gave sodium salt of *N*,*O*-sulfated DAC-95 (yellowish powder, 85% yield; DS = 1.4, based on the elemental analysis. Found: C, 23.07%; H, 4.38%; N, 4.55%; S, 14.27%). IR (KBr) 3600–3400 (NH_2, OH), 2900 (CH), 1650, 1320 (amide), 1250 (S=O), 1080 (C–O–C), 810 cm^{-1} (C–O–S); ^1H NMR (D_2O): δ 2.07 (0.15 H, s, N-Ac), 3.2–4.5 (6 H, m, C2–C6 protons), 4.6–5.2 ppm (1 H, m, C1 proton); $M_n = 27.1 \times 10^4$.

Partially 2-hydroxyethylated 92% deacetylated chitin (*O*-2-HE-DAC-92) was prepared by the modified method of Yamada et al. (Yamada and Imoto, 1981). The addition of 1 M NaOH to DAC-86 (2.0 g, 12 mmol as glucosamine residue) in 2 wt% aqueous acetic acid (200 ml) produced the precipitate, which was suspended in 3.7 M NaOH (50 ml). After cooling in an ice bath, ethylene chlorohydrin (3.9 g, 5 equivalent relative to glucosamine residue) was added to the suspension. The reaction mixture was stirred at 0°C for 1 h and then at 36°C for 18 h. After centrifugation, undissolved materials were washed with acetone, suspended in water (80 ml), and dialyzed to give *O*-2-HE-DAC-92 as a colorless powder (1.9 g, 85% yield; DS = 0.4, based on the ^1H NMR analysis). IR (KBr) 3500–3400 (NH_2, OH), 2900 (CH), 1680 (C–N–C), 1650, 1320 (amide), 1080–1040 cm^{-1} (C–O–C); ^1H NMR (D_2O, one drop of 20% DCl): δ 2.10 (0.24 H, s, N-Ac), 2.7–3.0 (0.9 H, m, C2 proton), 3.7–4.3 (7.1 H, m, C3–C6 protons and O–CH_2CH_2O), 4.9–5.0 ppm (1 H, m, C1 proton), $M_n = 4.45 \times 10^4$.

Partially *O*-methyl-*N*-trimethylated 86% deacetylated chitin chloride (*O*-Me-*N*-TM-DAC-86) was prepared as follows. Quaternization of amino group and *O*-methylation of DAC-86 was carried out according to Domard's method (Domard et al., 1986). After DAC-86 (2.0 g, 12 mmol as glucosamine residue) was dispersed in *N*-methyl-2-pyrrolidone (100 ml) overnight at room temperature, an aqueous solution (10 ml) containing NaOH (1.2 g, 30 mmol) and NaI (2.5 g, 16.7 mmol) was added to the DAC-86 suspension and then CH_3I (25.6 g, 15 equivalent relative to the glucosamine residue) was added. After stirring at 36°C for 8 h, the addition of ethanol (100 ml) to the reaction mixture produced the precipitate, which was redissolved in water (20 ml). This aqueous solution was treated by anion-exchange resin (40 ml, Amberlite IR-45, Cl^- type), dialyzed, and lyophilized to give *O*-Me-*N*-TM-DAC-86 as a colorless powder (2.2 g, 90% yield; DS of N-TM: 0.4, based on the ^1H NMR analysis (Domard et al., 1987)). IR (KBr) 3500–3400 (NH_2, OH), 2900, 2860 (CH), 1660, 1560 (amide), 1080 cm^{-1} (C–O–C); ^1H NMR (D_2O): δ 2.06 (0.4 H, s, N-Ac), 2.9–3.0 (0.4 H, m, C2 proton), 3.15 (3.8 H, s, $-N^+Me_3$), 3.3–3.4 (0.7 H, m, 3, 6-*O*-CH_3), 3.7–4.2 (5.5 H, m, C2–C6 protons), 4.9–5.1 ppm (1H, m, C1 proton); $M_n = 3.25 \times 10^4$.

2.2. Preparation of tablets and determination of electric resistance

The tablets (ca. 150 mg, 13 mm in diameter, and ca. 1 mm in thickness) of chitosan derivatives were prepared by the direct compression at 400 kg cm^{-2} for 10 min. The tablets containing various metal chlorides were prepared as follows. DAC-86 (100 mg, 0.60 mmol as hexosamine residue) and acetic acid (36 mg, 0.60 mmol, 1 equivalent to hexosamine residue) were added to an aqueous solution (10 ml) of metal chlorides (8.5–25.5 μmol). After stirring at room temperature for 1 h, the mixture was lyophilized to give the solid, which was used for the direct compression. In the case of metal sulfates, an aqueous solution (10 ml) of metal sulfates (1.7 mmol) was added to DAC-86 (400 mg) in 0.5% (w/v) aqueous acetic acid solution (30 ml). The precipitate formed was washed with acetone and dried in vacuum to give the solid, a part of which was used for the direct compression. Electrodes on the tablets were made with silver paste. The electrode distance on the tablet was 0.5 cm as shown in Fig. 2. The dry weight (W_0) of tablets was determined after drying under reduced pressure (10 mmHg) at 60°C for 24 h. The weight of tablet was equilibrated at the prescribed temperature and relative humidity (RH) in an environmental chamber (LH-20, Nagano Science Ltd.). After the determination of electric resistance, weight

Table 1
Effect of pressure and tablet weight on specific resistance (ρ) of DAC-86 tablets

Pressure (kg cm^{-2})	Tablet weight (mg)	Thickness (cm)	H_2O content (%)	log ρ
200	200	0.12	9.5 ± 0.1[a]	8.31 ± 0.0[a]
300	200	0.12	9.2 ± 0.2	8.35 ± 0.1
400	140	0.09	8.9 ± 0.2	8.38 ± 0.1
400	200	0.12	9.2 ± 0.2	8.37 ± 0.1
400	260	0.16	9.1 ± 0.3	8.33 ± 0.1
400	320	0.21	9.0 ± 0.3	8.35 ± 0.1
600	200	0.12	8.9 ± 0.1	8.46 ± 0.1

Condition: temperature, 20°C, RH, 50%.
[a] ± : Mean standard deviation ($n = 3$).

(W_t) and thickness of the tablets were determined. The water content (H (%)) was calculated by

$$H = 100(\Delta W/W_0)$$

where ΔW is the increasing weight of tablet by water sorption ($W_t - W_0$ (mg)).

After charging by DC 100 V for 1 min, the electric resistance of tablet was measured by an ohmmeter (Ultra Megohmmeter SM-8210, TOA Electronics Ltd.). The value of specific resistance (ρ) was calculated by

$$\rho = r(wh/d)$$

where ρ is specific resistance (Ω cm), r the electric resistance (Ω), w the width of electrode (cm), h the thickness of tablet (cm), and d the electrode distance (cm).

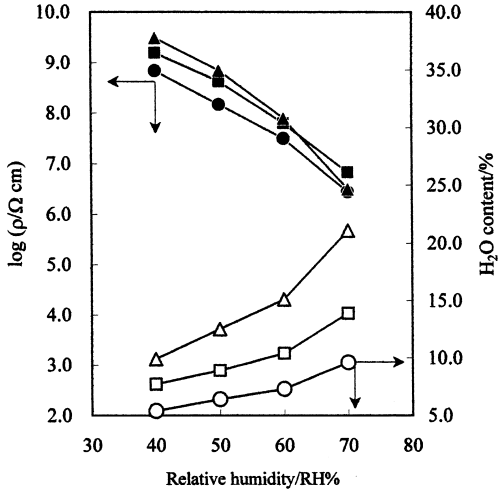

Fig. 3. Effect of relative humidity on specific resistance (ρ) of ACD tablets at 20°C.

Specific resistance	H_2O content		Tablet weight (mg)	Thickness (cm)
●	○	DAC-21	152	0.10
▲	△	PAC-50	146	0.10
■	□	DAC-86	156	0.10

3. Results and discussion

3.1. Estimation of specific resistance of chitosan samples by use of tablet

Taking the utilization as antistatic material for the functional textile into consideration, the specific resistance of many chitosan derivatives should be easily measured under various temperature and moisture conditions. When we tried to determine the specific resistance of chitosan films, it was very hard to obtain significant data, because the form and thickness of the film samples were rather affected by the relative humidity. We found that tablets made by direct compression of chitosan samples were very convenient for the simple and swift estimation of the specific resistance. As shown in Table 1, we examined the influence of the amount of DAC-86 (140–320 mg) and pursuer (200–600 kg cm^{-2}) for the preparation of tablets. In every case tested, both the water content and specific resistance (ρ) were nearly constant and independent on the pressure for the direct compression and weight of the tablets. Therefore, all tablets in the following experiments were prepared by the direct compression at 400 kg cm^{-2} using 140–320 mg of chitosan derivatives. In addition, DAC-86 tablets (150 mg) prepared from powder of various sizes (< 75, 75–150, 150–250, and > 250 μm) showed similar water content values (8.3%–9.4%) and log ρ values (8.7–9.0) at 20°C and RH = 50%. These results mean that tablets made by the prescribed method are useful for the study on the electric resistance.

3.2. Effect of temperature and water content on the specific resistance of acetylated chitosan derivatives

Before the study of the influence of ionic groups, we investigated the relation of water content, temperature, and the specific resistance of chitosan samples. Fig. 3 shows the relation between the water content and the specific resistance of DAC-86, PAC-50, and DAC-21. The water content in the tablet was controlled by varying the RH values, while water content values of the PAC-50 tablet were higher than those of other tablets. The ρ value decreased with an increase in the water content. The

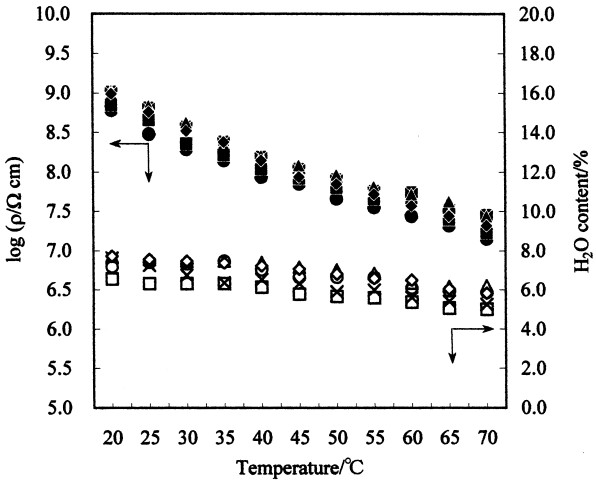

Fig. 4. Effect of temperature and DAC-86 weight on specific resistance (ρ) of DAC-86 tablet at RH, 40%.

Specific resistance	H_2O content	DAC-86 (mg)	Thickness (cm)
●	○	140	0.09
■	□	168	0.10
⊠	×	236	0.16
▲	△	284	0.19
◆	◇	318	0.21

PAC-50 tablet at RH = 40%, the DAC-86 tablet at RH = 55%, and the DAC-21 tablet at RH = 70% showed the almost same water content (ca. 10%), however the ρ values of these tablets decreased in this order. This phenomenon would suggest that the amount of acetamide group and its distribution in acetylated chitosan derivatives (ACD) molecule are important factors to control the electric resistance of ACD tablet. In addition, both the water content and the ρ value gradually decreased with an increase in the temperature (Fig. 4). When temperature rises from 25°C to 70°C, the dissociation constant of water (K_w) increases from $10^{-13.997}$ to $10^{-12.800}$ (Maeda et al., 1987). Hence, an increase in the amount of ionic carrier with increasing temperature results in decreasing the specific resistance in spite of a decrease in the water content.

Based on the results and discussion mentioned before, chitin and chitosan derivatives and various additives were investigated in the following section from the viewpoint of the amount of ionic carriers.

3.3. Effect of ionic species added and ionic character of polymer chain

When DAC-86 was transformed to its acetate form, the log ρ shown in Table 2 was decreased, because the amount of H^+ increased. The log ρ values of tablets containing metal chlorides (Cl^- = 25.5 μmol; Runs 3–8) were lower than that of the tablet containing no metal chloride (Run 2). The idea that the amount of ionic carriers seems to be a determining factor for the electric conduction was supported by the result that the log ρ values of the tablets decreased in the following order: DAC-86 tablet, DAC-86 acetate tablet, DAC-86 acetate tablets containing metal chlorides.

In contrast, DAC-86 acetate tablets containing metal sulfates (600 μmol; Runs 12–14) exhibited higher log ρ values than the tablet containing no metal sulfate (Run 2), although the amount of metal sulfate added was more than

Table 2
Specific resistance and water content of various ACD derivative tablets

Run	Sample	Salt[a]	DS[b]	H_2O content (%)	log ρ
1	DAC-86	—	—	7.7	9.2
2	DAC-86 acetate	—	—	10.4	7.4
3	DAC-86 acetate	KCl	—	13.1	6.5
4	DAC-86 acetate	$CaCl_2$	—	13.2	6.9
5	DAC-86 acetate	$AlCl_3$	—	13.4	6.7
6	DAC-86 acetate	$MnCl_2$	—	12.1	7.0
7	DAC-86 acetate	$FeCl_2$	—	12.6	6.8
8	DAC-86 acetate	$CuCl_2$	—	13.0	6.7
9	DAC-86 acetate	$MnSO_4$	—	17.3	10.0
10	DAC-86 acetate	$FeSO_4$	—	15.3	8.2
11	DAC-86 acetate	$CuSO_4$	—	14.3	9.7
12	PAC-50	—	—	9.9	9.5
13	*N*-Me-DAC-86	—	0.4	10.9	9.5
14	*N*-Pr-DAC-86	—	0.8	8.4	10.1
15	*N*-Bu-DAC-86	—	0.9	6.4	10.2
16	*O*-2-HE-DAC-92	—	0.4	4.5	9.2
17	*N*-CM-DAC-86 [H^+]	—	0.4	12.6	9.4
18	*N*-CM-DAC-86 [Na^+]	—	0.4	17.3	6.7
19	*N,O*-Sulfated DAC-95 [Na^+]	—	1.4	9.5	6.1
20	*O*-Me-*N*-TM-DAC-86 [Cl^-]	—	0.4	10.8	6.8

Tablet: ca. 150 mg, thickness ca. 0.12 cm; measure condition: 100 V, 1 min, 20°C, RH = 40%.
[a] Metal salt: MCl = 25.5 μmol, MCl_2 = 12.8 μmol, MCl_3 = 8.5 μmol, MSO_4 = 600 μmol.
[b] DS: degree of substitution.

24 times greater than that of metal chlorides added in Table 2. This phenomenon was explained by the difference in the distribution of water existing in the polymer chains. Because DAC-86/metal sulfate was precipitated by the cross-linking of polymer chains with metal sulfates added, this precipitate would contain water heterogeneously. Only small amount of water would be in the region where the polymer chains were relatively tightly combined with each other by the cross-linking though sulfate ion. Therefore, large amount of absorbed water in DAC-86/metal sulfate might not homogeneously distribute and this heterogeneity is disadvantageous for the movement of ionic carrier.

In order to expand of the distance between the polymer chain, we investigated chitosan derivatives having various substituents. As shown in Table 2, DAC-86 derivatives with non-ionic substituents such as *N*-Me-, *N*-Pr-, and *N*-Bu-DAC-86 did not improve the specific resistance. Among these tablets, the log ρ values increased with an increase in the hydrophobic character of the *N*-substitutent. Next, we examined *O*-2-HE-DAC-92, whose side chain has a hydrophilic group, hydroxy group. But the 2-hyroxyethyl substituent was not effective to obtain better specific resistance.

Finally the effect of ionic substituents on the specific resistance of DAC derivatives was investigated (Runs 18–20 in Table 2). The tablet of polyionic DAC derivatives such as DAC-86 acetate, *N*-CM-DAC-86, *N*,*O*-sulfated DAC-95, and *O*-Me-*N*-TM-DAC-86 exhibited the lower log ρ values compared with those of non-ionic materials such as DAC-86, PAC-50, *N*-Me-DAC-86, *N*-Pr-DAC-86, *N*-Bu-DAC-86, *O*-2-HE-DAC-92 in Table 2. This result indicates that ionic substituents of chitosan increased not only the amount of water kept among of polymer chain but also the amount of ionic carrier. Of special interest in Table 2 is that the specific resistance of polyionic derivatives (Runs 18–20) was comparable with that of DAC-86 acetate doped with metal chlorides (Runs 3–8). Therefore, the utilization of ionic substituents provides a new method to construct excellent antistatic materials which does not contain acidic dopant and inorganic salts that would be easily lost by dissolution in water. The tablet of *N*-CM-DAC-86 (Na^+) showed lower log ρ value compared with that of *N*-CM-DAC-86 (H^+), because of the higher ionic character. Therefore, these ionic derivatives of chitosan might be regarded as solid polyelectrolytes.

4. Conclusion

The effect of the water content and the degree of deacetylation on the specific resistance of chitosan derivatives was easily estimated by using the tablets made by direct compression. Especially, chitosan derivatives having ionic substituents such as *N*-CM-, *O*-Me-*N*-TM-, and *N*,*O*-sulfated DAC showed the smaller specific resistance (10^6 – 10^7 Ω cm) without the addition of dopant such as acetic acid and metal salts. To the best of our knowledge, chitosan derivatives having ionic substituents were investigated from the viewpoint of antistatic property for the first time and were expected as promising functional materials.

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