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Effects of acidic functional groups on dielectric properties of sodium alginates and carrageenans in water

Shuntaro Tsubaki[a,*], Masanori Hiraoka[a,b], Shingo Hadano[c], Kei Okamura[d], Tadaharu Ueda[c], Hiroshi Nishimura[e], Keiichiro Kashimura[e,1], Tomohiko Mitani[e]

[a] Oceanography Section, Science Research Center, Kochi University, Akebono-cho 2-5-1, Kochi 780-8520, Japan
[b] Usa Marine Biological Institute, Kochi University, Inoshiri, Usa, Tosa, Kochi 781-1164, Japan
[c] Department of Applied Science, Faculty of Science, Kochi University, Akebono-cho 2-5-1, Kochi 780-8520, Japan
[d] Center for Advanced Marine Core Research, Kochi University, B200 Monobe, Nankoku, Kochi 783-8502, Japan
[e] Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji 611-0011, Japan

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ABSTRACT

This study investigated the dielectric properties of sodium alginates and carrageenans in water at frequencies between 100 MHz and 20 GHz in regard to water-hydrocolloid interactions via acidic functional groups. Both sodium alginates and carrageenans showed conduction loss at lower frequencies and dielectric loss at higher frequencies. Reduction and desulfation of sodium alginates and carrageenans, which decreased the numbers of acidic functional groups, decreased their conduction loss. In addition, H^+-form carrageenans showed the highest ionic conduction. Correlational analysis of dielectric properties and related physical parameters showed that the loss tangent (tanδ) of the hydrocolloid solution was determined by the conductivity of the aqueous solution. Especially at pH below 2, strong H^+ conduction was associated with high tanδ probably due to the Grotthuss mechanism. The molecular dynamics of free water and H^+, viscosity conditions were also suggested to be associated with dielectric property of water-hydrocolloid system.

1. Introduction

Microwaves are widely utilized in cooking ovens around the world and are also utilized in radar and telecommunication devices as well as in industrial heating devices. Microwaves have a high heating rate due to their internal and direct heating of irradiated material. The efficiency of microwave heating of materials is dependent on their dielectric properties. In heating liquids, a combination of dielectric and conduction loss of solvent and solute mixtures determines the heating efficiency (Gabriel, Gabriel, Grant, Halstead, & Mingos, 1998). For example, microwave irradiation can more efficiently heat salt water than pure water (Tanaka & Sato, 2007), because electrolytes in salt water initiate ionic conduction in addition to the dielectric loss of water molecules, whereas pure water is heated only by dielectric loss.

Hydrocolloids are important products used in food and medicine, as well as industrially (Funami, 2011). Algal hydrocolloids, also called phycocolloids, have unique rheological properties and health promoting effects (Mabeau & Fleurence, 1993). More recently, algal hydrocolloids have been utilized as biomass feedstocks to produce biofuels and chemicals, due to their high net production per unit volume (Daroch, Geng, & Wang, 2013; Wei, Quarterman, & Jin, 2013). Algae produce a wide variety of species-specific hydrocolloids. For example, brown algae (Phaeophyceae) construct a matrix of polysaccharides containing alginate and fucoidan; red algae (Rhodophyceae) produce sulfated galactans such as carrageenan, agar and porphyran; and green algae (Chlorophytae), such as *Ulva* spp., accumulate starch and sulfated polysaccharides containing rhamnose and glucuronic acid, called ulvan (Lahaye & Robic, 2007).

Microwave heating has been utilized for the extraction, hydrolysis, pyrolysis and liquefaction of algal biomasses (Wang et al., 2011; Rodriguez-Jasso, Mussatto, Pastrana, Aguilar, & Teixeira, 2011; Cancela, Maceiras, Urrejola, & Sanchez, 2012; Quitain, Kai, Sasaki, & Goto, 2013; Tsubaki et al., 2014a). Microwaves can directly affect the high water and electrolyte content in algae, suggesting that microwave heating is highly compatible with

* Corresponding author. Tel.: +81 88 844 8927; fax: +81 88 844 8927.
E-mail addresses: stsubaki@kochi-u.ac.jp, shuntaro.tsubaki@gmail.com (S. Tsubaki).
[1] Present address: Chubu University, 1200 Matsumoto-cho, Kasugai, Aichi 487-8501, Japan.

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thermal conversion processes of algae. Algal hydrocolloids contain large numbers of acidic functional groups. Alginates are a type of polyuronate containing carboxylic groups, and fucoidan, carrageenan and agar contain sulfate groups (Wei et al., 2013). Ulvan contains both uronic acid and sulfate groups. We recently reported that the presence of sulfate groups in hydrocolloids from *Ulva meridionalis* (ulvan) and *Monostroma lattisimum* (rhamnan sulfate) may improve their dielectric properties by initiating ionic conduction (Tsubaki et al., 2014b).

In this study, we analyzed the dielectric properties of sodium alginates and carrageenans in water to assess the effects of acidic functional groups. Physical parameters, including conductivity, dynamics of free water, degree of hydration and viscosity, were also analyzed, as were their correlation with the dielectric properties of these solutions in order to understand the molecular mechanisms involved in the dielectric properties of algal hydrocolloid-water systems. Finally, the efficiency of microwave heating of these systems was assayed by determining the half-power depth of microwaves.

2. Materials and methods

2.1. Materials

Sodium alginates of different viscosities (cp. 80–120 and cp. 300–400, called "L" type and "M" type), λ- and κ-carrageenan, *Citrus* pectin and corn starch were purchased from Wako Pure Chemical Industries, Ltd., (Osaka, Japan) and used without further purification.

2.2. Reduction of sodium alginates

Sodium alginates were reduced as described (Fujihara & Nagumo, 1986). Briefly, each sodium alginate was allowed to react with 1-ethyl-3-(3-dimethylaminopropenyl) carbodiimide (EDC, Wako Pure Chemical Industries, Ltd.), while maintaining the pH of the solution at 4.75 by the addition of 0.1 M HCl. Sodium borohydrirde ($NaBH_4$, Wako Pure Chemical Industries, Ltd.) was added and the solutions incubated for 2 h at 50 °C. After cooling in an ice bath, excess amounts of $NaBH_4$ were removed by the addition of 3 M H_2SO_4, followed by dialysis and lyophilization. Degrees of reduction of sodium alginates were determined by the *m*-hydroxydiphenyl method using galacturonic acid as a calibration standard, with these results normalized to that of native L-type sodium alginate.

2.3. Ion exchange and desulfation of carrageenans

Ion exchanges of carrageenans were performed as described (De Araújo et al., 2013). Briefly, a strong cation exchange resin DOWEX 50W × 8 (H^+-form, Wako Pure Chemical Industries, Ltd.) was suspended in aqueous solutions of carrageenans (0.5 wt%) and stirred for 45 min at room temperature to produce H^+-form carrageenans. The ion exchange resin was filtered out and the supernatants lyophilized. Carrageenans were desulfated using the method described (Miller & Blunt, 1998). Briefly, carrageenan was added to dehydrated dimethylsulfoxide at 90 °C and stirred until the mixture became homogeneous. Pyridine and Sb_2O_3 were added to the solution and allowed to react for 3 h; the solution was subsequent cooled and poured into an aqueous solution of $NaHCO_3$. The resulting solution was dialyzed and lyophilized. The degree of desulfation was monitored by FT–IR from 400 to 4000 cm^{-1} by the KBr method at 4 cm^{-1} resolution (FT–IR 6200, Jasco Co. Tokyo, Japan).

2.4. Dielectric measurement of hydrocolloids in water and analysis of related physical parameters

The relative permittivity and loss factor of aqueous solutions (0.5, 1.0 and 2.0 wt%) of sodium alginates, carrageenans, corn starch and *Citrus* pectin were measured at 27 °C, 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C by the coaxial probe method using an Agilent Technologies 5242A Network Analyzer and an Agilent high temperature probe in a range of 100 MHz to 20 GHz (Agilent Technologies Inc.), as described (Tsubaki et al., 2014b). The dielectric loss tangent ($\tan\delta$) was calculated using the equation;

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \quad (1)$$

where ε' and ε'' are the relative permittivity and dielectric loss, respectively. All results are the means of triplicate determinations. The dielectric dispersion of free water was further characterized by the Cole–Cole equation (Gabriel et al., 1998):

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}} \quad (2)$$

where ε^*, ε_s, ε_∞, j, ω, τ, and α are the relative permittivity and loss factor, the static frequency, the infinite frequency, an imaginary unit, the angular frequency, the relaxation time and the distribution parameter, respectively. The half-power depth (D) of each hydrocolloid solution was calculated using the equation (Singh & Heldman, 2009):

$$D(\text{cm}) = \frac{3.31 \times 10^9}{f\sqrt{\varepsilon'} \times \tan\delta} \quad (3)$$

where f is frequency.

The DC conductivity of the solutions were measured using an electric conductive meter (ES-51, Horiba, Ltd., Kyoto, Japan) and their pH measured using a pH meter (Seven Go pH meter, Mettler-Toredo, OH, USA). The concentrations of Na^+ and K^+ were determined using ICP-AES (Optima 4300 DV CYCRON, PerkinElmer Inc. MA, USA), and viscosity was determined by viscometry by using a VM-10AL (Sekonic Co. Tokyo, Japan) at 23 °C.

2.5. DSC analysis of hydrocolloids in water

The amount of non-freezable water was analyzed by DSC (SII Exstar 6200, Hitachi High-Tech Science Co., Tokyo, Japan) as described (Yudianti, Karina, Samkamoto, & Azuma, 2009), with modifications. DSC thermograms of hydrocolloid in water (0.5, 1.0 and 2.0 wt%) were obtained from −30 °C to 50 °C at a heating rate of 8 °C min^{-1} in a sealed aluminum pan, with an empty sealed aluminum pan used as a reference. The amount of non-freezing water was calculated from the ratio of endothermic peaks areas of hydrocolloid solutions to those of pure water using the equation (Yudianti, Karina, Sakamoto, & Azuma, 2009):

$$W_b(\%) = W_r - 100 \times \left(\frac{Q_{\text{endo}}}{Q_{\text{pure}}}\right) \quad (4)$$

where W_b and W_r are the amounts of non-freezable and equilibrium water, respectively, and Q_{endo} and Q_{pure} are the enthalpy of hydrocolloid solution and pure water (ΔH = 372 J g^{-1}), respectively.

2.6. Microwave heating characteristics of the hydrocolloids in water

Microwave heating characteristics of hydrocolloids in water were determined by heating in a microwave oven (Start D, 2.45 GHz, Milestone, Inc., CT, USA) equipped with thermocouple thermometer and PID (Proportional, Integral and Derivative) temperature control with maximum output of 300 W. Aqueous

Table 1
Concentrations of H^+ and cations in native and derivatized 0.5 wt% sodium alginates L and M, λ- and κ-carrageenans, corn starch and pectin in water.

Sample	Derivatization	H^+ (mol L^{-1})	Na^+ (mol L^{-1})	K^+ (mol L^{-1})
Sodium alginate L	Native	5.62×10^{-8}	9.35×10^{-3}	2.17×10^{-4}
	Reduced	4.79×10^{-9}	1.52×10^{-3}	7.16×10^{-5}
Sodium alginate M	Native	7.24×10^{-8}	1.01×10^{-2}	1.43×10^{-4}
	Reduced	7.76×10^{-8}	3.09×10^{-3}	7.42×10^{-5}
λ-Carrageenan	Native	4.79×10^{-8}	2.69×10^{-3}	1.96×10^{-3}
	H^+-form	1.26×10^{-2}	5.59×10^{-4}	2.40×10^{-4}
	Desulfated	6.17×10^{-7}	5.38×10^{-3}	6.55×10^{-4}
κ-Carrageenan	Native	3.02×10^{-8}	1.04×10^{-3}	4.25×10^{-3}
	H^+-form	7.76×10^{-3}	1.86×10^{-4}	2.71×10^{-4}
	Desulfated	1.82×10^{-6}	1.76×10^{-3}	1.25×10^{-4}
Corn starch	Native	2.51×10^{-6}	6.55×10^{-5}	4.35×10^{-5}
Citrus pectin	Native	4.57×10^{-4}	6.35×10^{-4}	8.18×10^{-5}

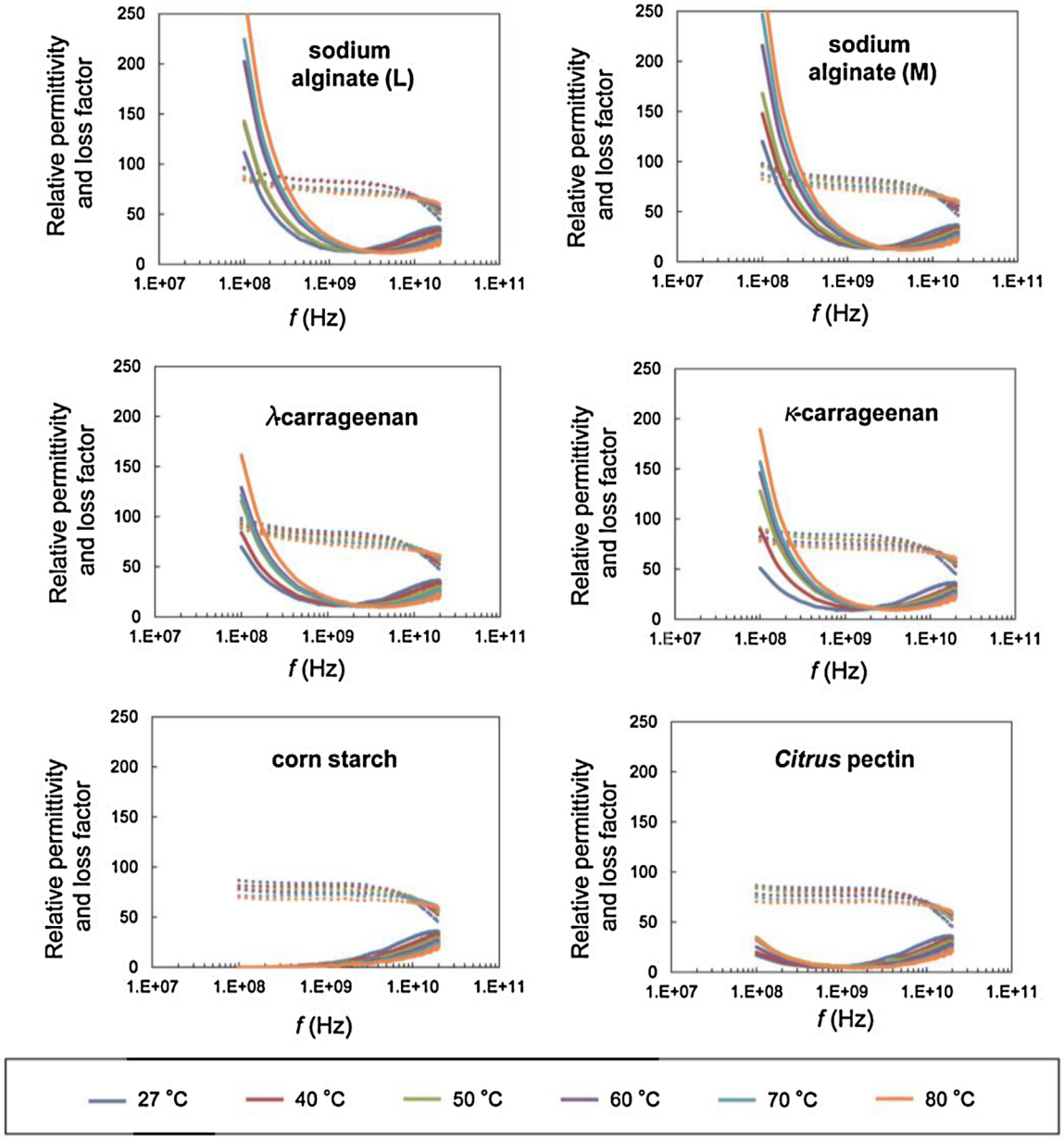

Fig. 1. Temperature dependency of the dielectric spectra of native sodium alginates L and M, λ- and κ-carrageenans, corn starch and *Citrus* pectin in water (2.0 wt%). The dashed lines represent relative permittivity and the solid lines represent the loss factors.

solutions of hydrocolloids (0.5, 1.0 and 2.0 wt%) were microwaved using PTFE-made HPR-100 reactor under closed conditions, with the temperature increasing over 4 min to 140 °C, followed by cooling in ice bath. The microwave power consumption (Q_{MW}) was estimated from the oven's microwave output monitor. The total number of calories absorbed by the solution (Q_{TH}) was calculated as (Moseley & Kappe, 2011):

$$Q_{TH} = mc_p\Delta T \quad (5)$$

where m and c_p are the mass of the irradiated medium (kg) and the specific heat capacity, respectively. The heat capacity of water (4.154×10^3 J kg^{-1} K^{-1}) was used in this study due to predominance of water in the solution. The energy efficiency of microwave heating could then be calculated as (Moseley and Kappe, 2011):

$$\text{Energy efficiency}(\%) = 100 \times \left(\frac{Q_{MW}}{Q_{TH}}\right) \quad (6)$$

3. Results and discussion

3.1. Derivatization of sodium alginates and carrageenans

The effects of acidic functional groups on the dielectric properties of sodium alginates and carrageenans were evaluated by comparing native, reduced and desulfated alginates and carrageenans. Sodium alginates are composed of D-mannuronic acid and L-gluronic acid; their carboxylic groups were reduced by hydrogenolysis to produce sodium alginates with a lower degree of acidic functional groups (Fig. S1A). The reduction efficiencies of sodium alginates (L) and (M) were 53.6% and 43.0%, respectively. Carrageenans are typically β-(1 → 3) and β-(1 → 4) linked galactose and anhydrogalactose units, some of which are sulfated. The sulfate groups were removed by solvolysis to produce carrageenans with lower degrees of sulfation, with the degrees of desulfation monitored by FT–IR spectroscopy (Fig. S1B). The typical broad absorbance of carrageenans at 1250 cm^{-1}, due to the asymmetric and symmetric vibration of sulfate groups (Matsuhiro, 1996), was almost eliminated from κ-carrageenan, but λ-carrageenan still retained some sulfated groups. The difference in desulfation efficiency may be due to the higher degree of sulfation in native λ- than κ-carrageenan.

The counter ions of the carboxylic and sulfate groups are shown in Table 1. After reduction of sodium alginates, the concentrations of Na^+ decreased in proportional to the decrease in number of carboxylic groups. K^+ was the predominant counter ion on native carrageenans. Following treatment with an ion exchange resin, most of the K^+ and Na^+ was replaced by H^+. After desulfation treatment, the predominant counter ion became Na^+.

3.2. Temperature dependency of the dielectric properties of sodium alginates and carrageenans in water

The dielectric properties of aqueous solutions of native sodium alginates and carrageenans were analyzed at frequencies between 100 MHz and 20 GHz and at temperatures between 27 °C and 80 °C, with these results compared with those of corn starch and *Citrus* pectin. The typical dielectric spectra of these molecules are shown in Fig. 1. The loss factors of sodium alginates and carrageenans showed U-shaped curves, similar to those observed with acidic hydrocolloids extracted from *U. meridionalis* and *M. lattisimum* (Tsubaki et al., 2014b). The loss factors at lower frequency were due to conduction loss of acidic hydrocolloids and their counter ions. Sodium alginates showed higher ionic conduction than carrageenans, probably due to larger amounts of Na^+ (Table 1). Increases in temperature increased conduction loss due to higher ionic conductivity, resulting from the lower restriction of water molecules at elevated temperatures (Gabriel et al., 1998). In contrast, corn starch in water did not show ionic conduction, because corn starch does not contain acidic functional groups and their corresponding counter ions (Table 1). Only slight conduction loss was observed for *Citrus* pectin, due to the lower concentration of counter ions (Table 1). Pectin contains lower amounts of acidic monosaccharides, with the carboxylic groups in pectin sometimes further neutralized by methyl esterification or acetylation (Novosel'skaya, Voropaeva, Semenova, & Rashidova, 2000).

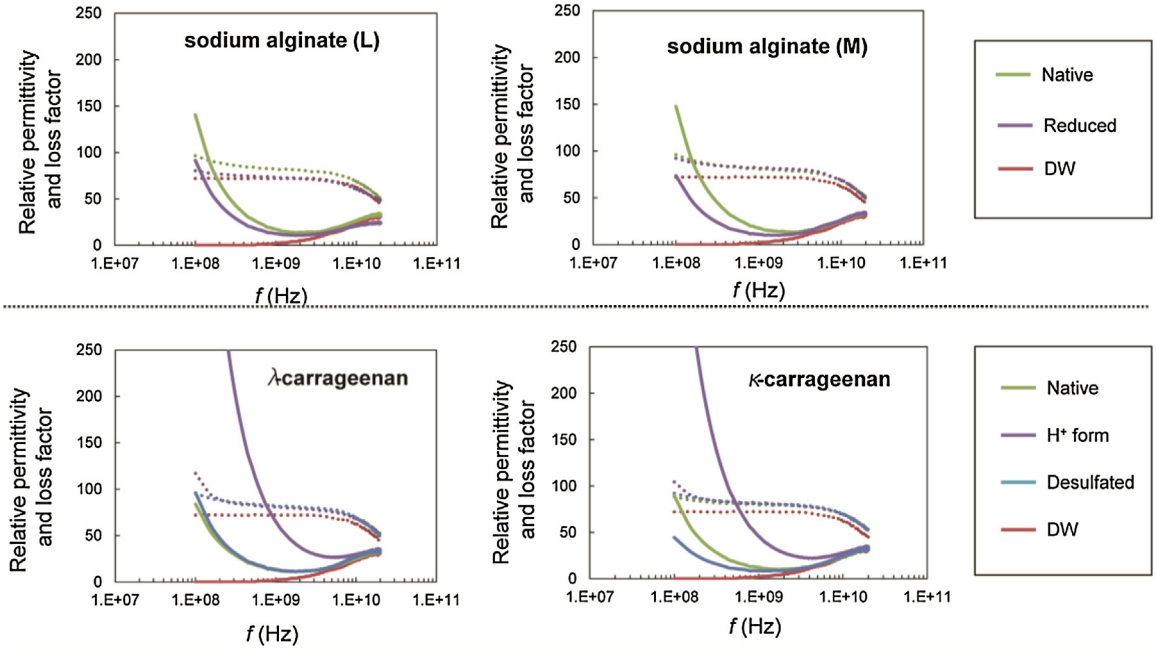

Fig. 2. Dependency of the dielectric spectra on acidic functional groups of sodium alginates L and M, λ- and κ-carrageenan, corn starch and *Citrus* pectin in water (2.0 wt%). The dashed lines represent relative permittivity, whereas the solid lines represent loss factors. DW; distilled water.

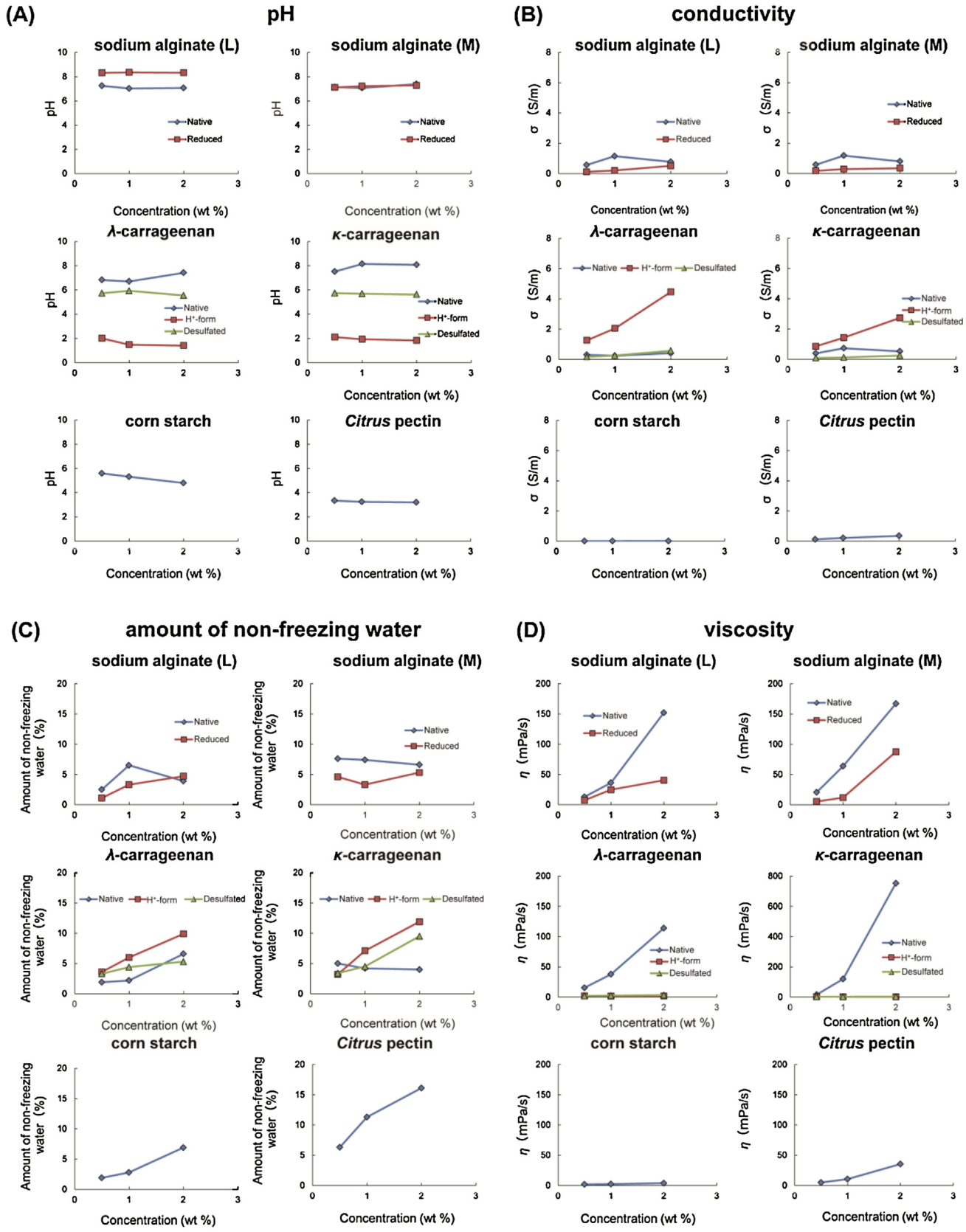

Fig. 3. Effects of concentrations of hydrocolloids on pH, conductivity, amount of freezing water and viscosity of 0.5, 1.0 and 2.0 wt% sodium alginates, carrageenans, corn starch and *Citrus* pectin in water.

Dielectric loss of free water was observed at frequencies above 10 GHz, with these peaks observed with all hydrocolloids tested. Generally, at room temperature, free water shows dielectric dispersion at around 20 GHz, corresponding to the cooperative relaxation of long range H-bond mediated dipole–dipole interactions (Fukasawa et al., 2005). The dielectric loss of water decreased as temperature increased, because higher temperatures increase the mobility of water molecules, reducing molecular friction (Gabriel et al., 1998; Okada, Yao, Hiejima, Kohno, & Kajihara, 1999). Simultaneously, dielectric dispersion peaks move to higher frequency.

Measurements of relative permittivity showed that the main dielectric relaxation of free water was above 10 GHz. Another small displacement was observed at frequencies around 100–200 MHz. This was probably due to the local chain motion of macromolecules, similar to proteins (Gabriel et al., 1998) and pullulan (Kishikawa et al., 2013) in water. This process may be hindered by strong ionic conduction in loss factor spectra. As the temperature increased, the relative permittivity decreased with decreases in the strength and extent of hydrogen bonding of water molecules.

3.3. Acidic functional group dependency of dielectric properties of sodium alginate and carrageenans

The effects of acidic functional groups on dielectric properties were investigated by comparing native and derivatized sodium alginates and carrageenans (Fig. 2). Reduction of sodium alginate M and desulfation of κ-carrageenan decreased their conduction losses. In contrast, λ-carrageenan did not show a decrease in conduction, probably because it still retains sulfate groups and counter ions (Fig. S1B). Ion exchanges of carrageenans from the native K^+-form to the H^+-form significantly increased ionic conduction. Native and derivatized hydrocolloids showed higher relative permittivity than pure water at all ranges investigated, due to kosmotropic effects resulting from the lower polarity of sugar molecules (Chandrasekaran, Ramanathan, & Basak, 2013).

3.4. Conductivities, water structures and viscosities of aqueous solution of sodium alginates and carrageenans

Due to the significant effects of ionic conduction on the dielectric spectra of algal hydrocolloids (Figs. 1 and 2), the pH and conductivity of these solutions were analyzed. Native and treated sodium alginates, carrageenans and corn starch all had pH values between 4 and 8 (Fig. 3A). The pH of the H^+-form of carrageenan was significantly lower than that of native and desulfated carrageenans. *Citrus* pectin also showed slightly weak acidity, because most of its counter ions are H^+ and Na^+.

Conductivities of the hydrocolloid solutions are shown in Fig. 3B. Native sodium alginates showed the highest conductivity, followed by carrageenans and *Citrus* pectin. Corn starch, however, showed no apparent conductivity. Reduction of sodium alginates and desulfation of κ-carrageenans decreased their conductivities, probably due to decrease in acidic functional groups and their counter ions. On the other hand, λ-carrageenan did not show significant decrease in conductivity as similarly observed in the dielectric measurements (Fig. 2). The conductivities of the H^+-form carrageenans were significantly higher, indicating that H^+ has a greater effect

Table 2
Relaxation times of free water and loss tangents (tanδ) at 2.45 GHz of aqueous solutions of 0.5, 1.0, and 2.0 wt% of native and derivatized sodium alginates (L and M), λ- and κ-carrageenans, corn starch and pectin.

Sample	Derivatization	Concentration (wt%)	τ (ps)	tanδ
Sodium alginate L	Native	0.5	7.7	0.126
		1.0	7.9	0.154
		2.0	7.9	0.173
	Reduced	0.5	7.5	0.115
		1.0	8.2	0.145
		2.0	7.8	0.164
Sodium alginate M	Native	0.5	7.8	0.152
		1.0	7.9	0.139
		2.0	7.9	0.183
	Reduced	0.5	7.8	0.129
		1.0	8.5	0.146
		2.0	8.0	0.171
λ-Carrageenan	Native	0.5	7.8	0.131
		1.0	7.8	0.136
		2.0	7.9	0.160
	H^+-form	0.5	8.0	0.189
		1.0	8.8	0.263
		2.0	9.0	0.421
	Desulfated	0.5	7.8	0.123
		1.0	8.5	0.149
		2.0	8.0	0.167
κ-Carrageenan	Native	0.5	8.1	0.138
		1.0	8.2	0.134
		2.0	7.9	0.152
	H^+-form	0.5	8.0	0.159
		1.0	8.4	0.216
		2.0	8.4	0.254
	Desulfated	0.5	7.8	0.113
		1.0	8.0	0.139
		2.0	8.4	0.140
Corn starch	Native	0.5	8.2	0.119
		1.0	8.0	0.112
		2.0	8.1	0.120
Citrus pectin	Native	0.5	8.2	0.127
		1.0	8.1	0.119
		2.0	8.1	0.128

than other cations on the conductivity of hydrocolloids in water, an effect called a proton jump or the Grotthus mechanism (Bonin, Costentin, Louault, Robert, & Savéant, 2011).

The degrees of hydration of hydrocolloids in water were estimated by DSC analysis of the amounts of non-freezing bound water. Typical thermograms are shown in Supplementary Fig. S2. Fig. 3C shows the amount of non-freezing water in aqueous hydrocolloid solutions. The reduction of sodium alginate slightly decreased the amount of non-freezing water, whereas the H^+-form and desulfated κ-carrageenan showed increased amounts of non-freezing water. Starch showed the lowest and *Citrus* pectin the highest amount of non-freezing water. Differences in the amounts of non-freezing water appears to be related to the numbers of acidic functional groups, the types of counter ions (H^+ or another metallic cation), and the degree of branching structures in the sugar chains. The acidic functional groups of sodium alginates and carrageenans and their counter ions may have enhanced hydrocolloid hydration. In contrast, the hydration of *Citrus* pectin may be related to the branching structure of the hydrocolloid as well as the carboxylic groups of galacturonic acids (Novosel'skaya et al., 2000).

The viscosity of the aqueous hydrocolloid solutions are shown in Fig. 3D. Reduction of sodium alginates decreased the viscosity of the solution. Native κ-carrageenan formed a gel at 2 wt% with very high viscosity and ion exchange significantly reduced its viscosity. Native λ-carrageenan did not form gel, however, the viscosity decreased by ion exchange and desulfation treatments as similarly observed for κ-type. Carrageenan is thought to form a gel network by aggregation of helix chains (Smidsrød & Grasdalen, 1982). The static repulsion of sulfate groups due to substitution of K^+ for H^+ may have decomposed the gel network and reduced the viscosity of the solution. At concentrations below 2 wt% corn starch and *Citrus* pectin were less viscous than algal hydrocolloids.

The dynamics of free water were determined by analyzing the relaxation time of water molecule using dielectric measurements. Table 2 shows the relaxation times of free water and the aqueous hydrocolloid solutions at 27 °C. The relaxation times of most of these solutions were almost the same as that of pure water (8.0 ps), however, the relaxation time of water in the H^+-form carrageenans solution showed longer value. The formation of hydrogen bonding due to higher H^+ concentration might have restricted dynamics of water molecule and gave longer relaxation time.

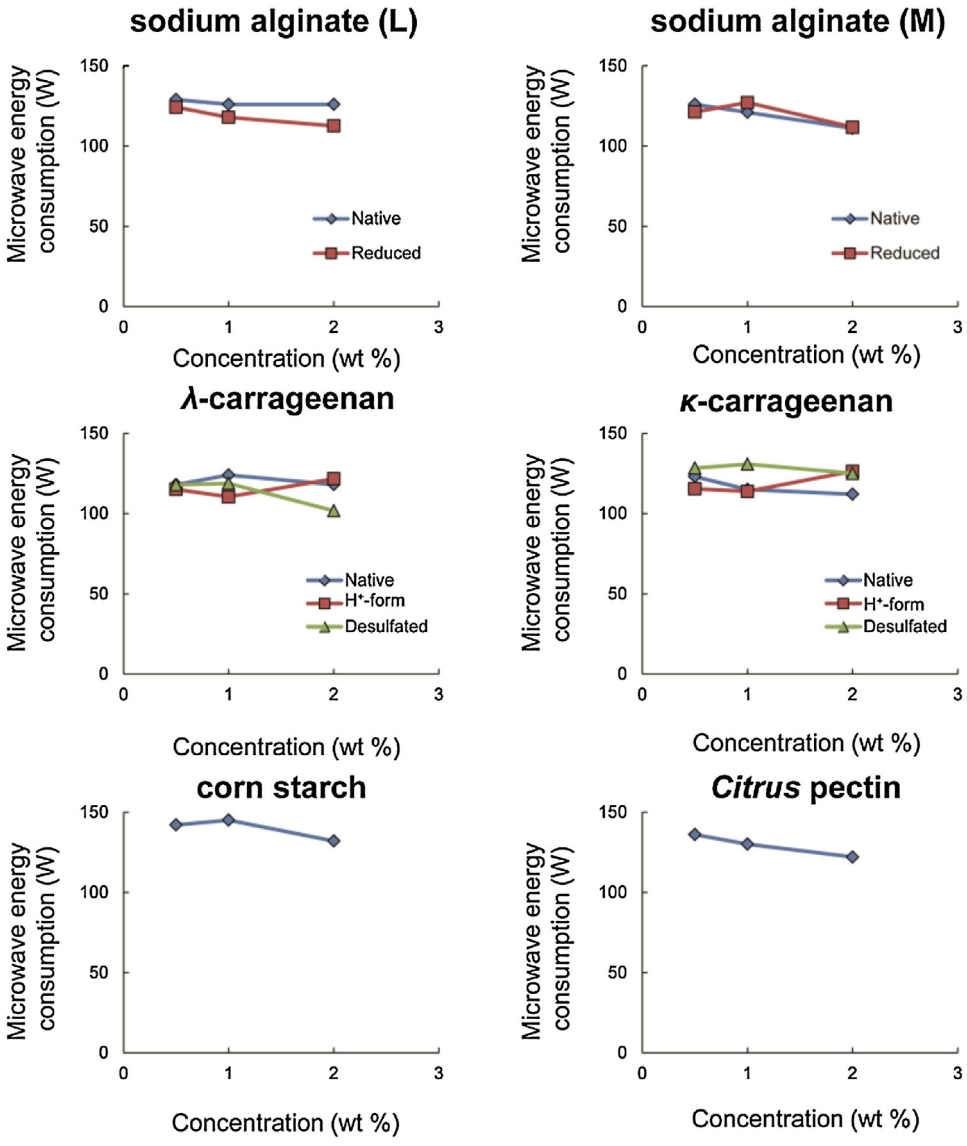

Fig. 4. Microwave energy consumption by 0.5, 1.0, and 2.0 wt% sodium alginate M, κ-carrageenan, corn starch and *Citrus* pectin in water.

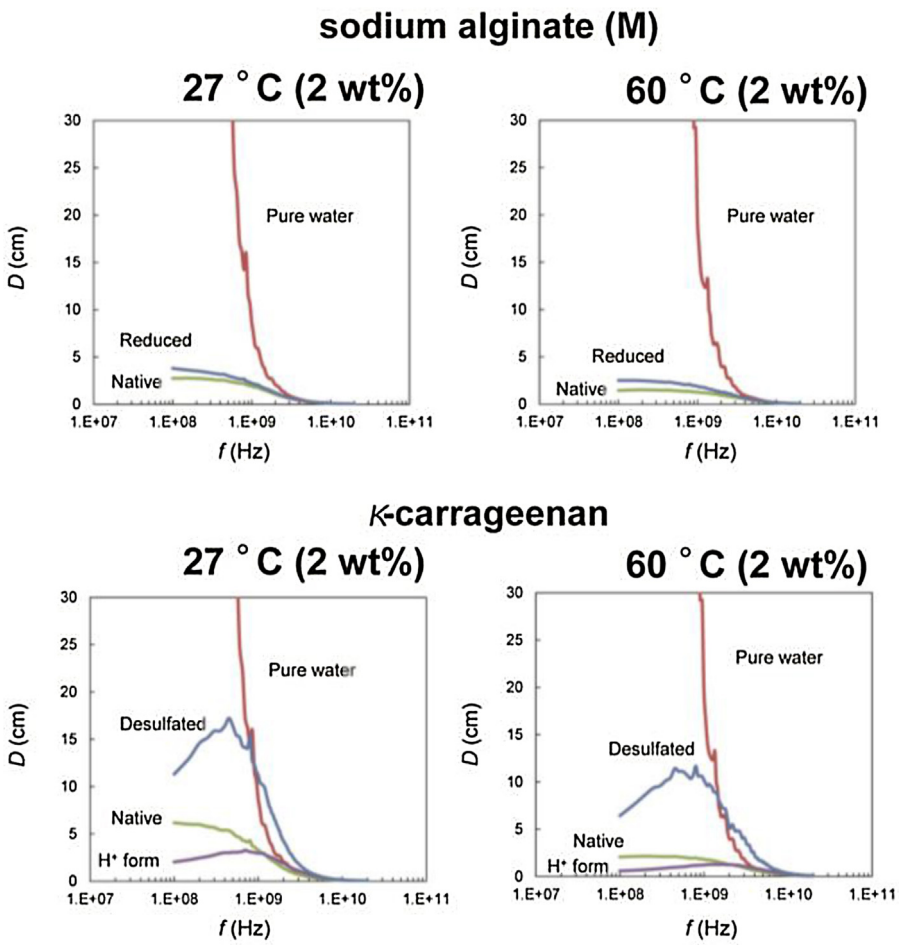

Fig. 5. Half-power depths of microwaves in 2 wt% sodium alginate M, κ-carrageenan and their derivatives in water.

3.5. Microwave heating efficiency and half-power depth of aqueous solutions of sodium alginates and carrageenans

The microwave heating efficiencies of hydrocolloids in water were evaluated by measuring tanδ at 2.45 GHz, as well as by measuring energy consumption and microwave half-power depth. The values of tanδ are listed in Table 2. Similarly to the loss factor in the dielectric spectra (Fig. 1), the reduction of sodium alginates and the desulfation of κ-carrageenan reduced tanδ. In contrast, the desulfation of λ-carrageenan did not show the same results as native λ-carrageenan due to its lower degree of desulfation (Fig. S2B). The tanδ of the H^+-form carrageenan was significantly higher, whereas the tanδ of corn starch and *Citrus* pectin were significantly lower, than those of algal hydrocolloids.

The microwave heating efficiencies of hydrocolloid solutions were evaluated by measuring the ratio of microwave energy input to the theoretical energy required to heat aqueous solutions (Fig. 4). Although tanδ values varied with the type of hydrocolloid, the energy efficiencies were about 30% to 40%. Not only their dielectric properties, but other factors, including the design of the microwave oven, microwave frequency, placement of material inside the oven and impedance matching were associated with microwave heating efficiency (Chandrasekaran et al., 2013).

The half-power depths of native and derivatized sodium alginate M and κ-carrageenan between 100 MHz and 20 GHz at 27 °C and 60 °C are shown in Fig. 5. The half-power depth of pure water increased as frequency decreased due to lower dielectric loss. In contrast, the half-power depths of aqueous hydrocolloid solution were lower than that of pure water because electrolyte compounds absorb microwave energy by ionic conduction, followed by its decay. Reduced sodium alginate M and desulfated κ-carrageenan were more transparent to microwaves than the native molecules because of their lower conduction loss. In contrast, the half-power depth of the H^+-form of κ-carrageenan was significantly lower. At 60 °C, the half-power depth of pure water increased due to the increased transparency of the water, whereas the half-power depths of hydrocolloid solutions decreased because ionic conduction become prominent at higher temperatures.

3.6. Correlations of tanδ of aqueous solutions of sodium alginate and carrageenan at 2.45 GHz with other physical properties

The correlations of tanδ with other physical parameters are shown in Fig. 6. Conductivity was significantly correlated with tanδ ($R = 0.94928$, $p \leq 0.01$ ($n = 36$); Fig. 6A), indicating that ionic conduction of acidic hydrocolloids was the predominant parameter determining their dielectric properties in water. Tanδ was markedly increased at pH's below 2, indicating that H^+ concentrations higher than 1.0×10^{-2} mol L^{-1} are required to initiate ionic conduction (Fig. 6B). H^+ showed higher conductivity in water than other electric charges because H^+ jumps through the hydrogen bond in aqueous solution by the Grotthuss mechanism.

Tanδ was also weakly associated with the relaxation of free water, being higher at greater relaxation times and suggesting that the restriction of water molecules initiates more friction in water molecule dynamics at 2.45 GHz. In contrast, the relationship between tanδ and non-freezing water, a type of bound water, was largely dependent on the type of polysaccharide. For example, the

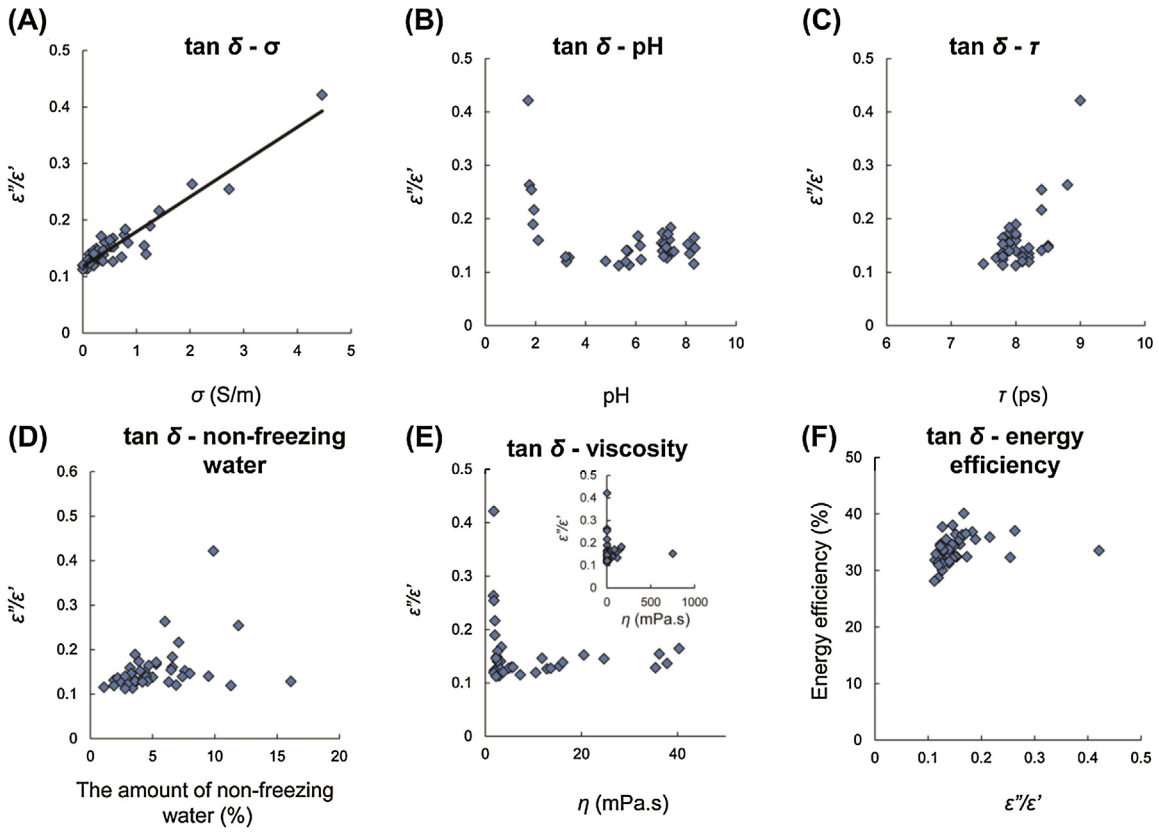

Fig. 6. Correlations between tanδ at 2.45 GHz with other physical properties of hydrocolloids in water, including (A) σ, (B) pH, (C) τ, (D) non-freezing water, (E) viscosity, (F) energy efficiency.

H^+-form of carrageenan showed a larger amount of non-freezing water with high tanδ. *Citrus* pectin was also associated with large amounts of non-freezing water, maybe due to the branching structures of the sugar chains, but the tanδ was relatively low.

The effects of viscosity on tanδ are shown in Fig. 6E. The H^+-form of carrageenans had a high tanδ, along with very low viscosity. The lower restriction of H^+ by surrounding water molecules may also contribute to faster H^+ conduction, a phenomenon similar to temperature-dependent ionic conduction. At elevated temperatures, ionic conduction became prominent with the decreased restriction of ions by surrounding water molecules (Fig. 1). These results suggested that the relationships between water and hydrocolloid systems via acidic functional groups are significantly associated with their dielectric properties.

Although high tanδ may be due to H^+ conduction, the maximum energy efficiency was 40.1% using a laboratory-scale microwave oven. This could be due to loss of heat from the reactor wall as well as lower half-power depth of hydrocolloid solutions with high tanδ. The lower microwave frequency was expected to have advantages in aqueous solutions of high tanδ.

4. Conclusion

This study assessed the dielectric properties and related physical parameters of algal hydrocolloids in water. Sodium alginates and carrageenans showed high ionic conduction, whereas corn starch and *Citrus* pectin showed no or only slight ionic conduction. Analysis of the correlations between the tanδ of the aqueous hydrocolloid solutions and related parameters showed that tanδ was determined mainly by ionic conduction. By changing the degree of substitution, acidic functional groups of algal hydrocolloids were shown to be related to the stimulation of ionic conduction. Especially in the case of carrageenans, the H^+-form type showed a significant increase in conduction loss due to high conductivity of H^+. In addition, a pH below 2 was required for good ionic conduction by H^+. Properties of water, such as the relaxation time of free water and the degree of hydration of hydrocolloid solutions, were associated with their dielectric properties. In addition, lower restriction of H^+ by surrounding water molecules at higher temperatures or lower viscosities facilitated H^+ conductivity. The half-power depth of the hydrocolloids in water suggested that lower microwave frequencies are needed to obtain the advantages of the effects of ionic conduction with better microwave penetration.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.08.092.

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