



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



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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<sup>+</sup>-form carrageenans showed the highest ionic conduction. Correlational analysis of dielectric properties and related physical parameters showed that the loss tangent ( $\tan\delta$ ) of the hydrocolloid solution was determined by the conductivity of the aqueous solution. Especially at pH below 2, strong H<sup>+</sup> conduction was associated with high  $\tan\delta$  probably due to the Grotthuss mechanism. The molecular dynamics of free water and H<sup>+</sup>, viscosity conditions were also suggested to be associated with dielectric property of water-hydrocolloid system.

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### 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

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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 laticimum* (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),  $\lambda$ - and  $\kappa$ -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 borohydride ( $\text{NaBH}_4$ , 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  $\text{NaBH}_4$  were removed by the addition of 3 M  $\text{H}_2\text{SO}_4$ , 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  $\times$  8 ( $\text{H}^+$ -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  $\text{H}^+$ -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  $\text{Sb}_2\text{O}_3$  were added to the solution and allowed to react for 3 h; the solution was subsequent cooled and poured into an aqueous solution of  $\text{NaHCO}_3$ . The resulting solution was dialyzed and lyophilized. The degree of desulfation was monitored by FT-IR from 400 to 4000  $\text{cm}^{-1}$  by the KBr method at 4  $\text{cm}^{-1}$  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  $\varepsilon'$  and  $\varepsilon''$  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  $\varepsilon^*$ ,  $\varepsilon_s$ ,  $\varepsilon_\infty$ ,  $j$ ,  $\omega$ ,  $\tau$ , and  $\alpha$  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-Torred, OH, USA). The concentrations of  $\text{Na}^+$  and  $\text{K}^+$  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  $\text{min}^{-1}$  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  $Q_{\text{endo}}$  and  $Q_{\text{pure}}$  are the enthalpy of hydrocolloid solution and pure water ( $\Delta H = 372 \text{ J g}^{-1}$ ), 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

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