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Ultrasound effect used as external stimulus for viscosity change of aqueous carrageenans

Josue Addiel Venegas-Sanchez, Tagaya Motohiro, Kobayashi Takaomi *

Department of Materials Science and Technology, Nagaoka University of Technology, Kamitomioka 1603-1, Nagaoka 940-2188, Japan

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ABSTRACT

Ultrasound (US) serves as a stimulus to change shear viscosity of aqueous polysaccharides of ι-carrageenan, κ-carrageenan and, agar. The US effect was compared in their aqueous solutions at 60 °C for the US frequency of 23, 45, and 83 kHz. Under the US condition with 50 W at 45 kHz, the shear viscosity of each aqueous solution was decreased significantly. Subsequently, when the US was stopped, the shear viscosity returned back to the original value. In addition, the US showed different effects of the US frequency over the viscosity change in the three kinds of polysaccharides. When the US frequency was changed, the US effects were less at 83 kHz and 28 kHz for the shear viscosity change. In addition, as NaCl was present in the aqueous solution, the viscosity change decreased by the US exposure. These results suggest that the US effect on the viscosity reduction was influenced by the condition of polymer coil conformation, which was expanded or shrank by electrostatic repulsion of the SO_3^- groups. FT-IR analysis supported that the hydrogen bonds of carrageenans were broken during the US exposure. Using Fourier self-deconvolution for the FT-IR spectra without and with US exposure suggests that the US influenced the hydrogen bonds of water and the OH group of polysaccharides.

1. Introduction

It has been well known that ultrasound (US) technique is applied in various fields such as engineering, medicine and other processes. Generally, US resource becomes to be mainly used to dissolve substances or homogenize mixtures at low-frequency. Therefore, US technique has earned interest in their operations [1,2]. Especially in sono-process, US irradiation related to the extraction in food engineering [3,4] and separation process like a membrane [5,6]. Also, few studies of smart materials have been developed in ultrasound sensitive materials as external trigger, although sensitive external trigger such as light, heat or electricity has been found [7]. In this case, US could behave as a stimulus in volume phase-transition of copolymer microgels of *N*-isopropyl acrylamide (NIPAM) and acrylic acid (AA) [8]. In addition, US irradiation significantly decreased the shear viscosity of the copolymer aqueous solutions [9], indicating the breaking of hydrogen bonding networks of the aqueous copolymer by lower frequency of US. In similar behavior of the low frequency US, hydrogen bonds in aqueous PAA/Al_2O_3 slurry were influenced by the US exposure [10]. These might be due to US absorption into the aqueous medium of hydrogen bonded polymers.

In contrast to these studies, the present work described US effect on aqueous viscosity for industrial applications of carrageenans and agar. These are kind of linear polysaccharides obtained from red seaweeds [11]. These polysaccharides exhibit a gelation behavior at 30–45 °C. Therefore, there are many industrial uses for example in jellies pudding of food industry and biotechnology. Especially κ-carrageenan and agar are important polysaccharides, when the medium temperature increases they became in viscous solutions [11–14] at over 60 °C. As shown in Scheme 1, chemical structure of agar consists in (1,3)-linked β-galactopyranose and (1,4)-linked (3,6)-anhydro-α-galactopyranose unit. In the case of κ-carrageenan, the repeated unit consists of (1,3)-linked galactopyranose 4-sulphate and (1,4)-linked 3,6-anhydrogalactopyranose residues and ι-carrageenan differs in the number of SO_3^- group [11]. It is known that both carrageenans were widely used as food additives to produce emulsion systems. Therefore, viscosity control of the viscous solution becomes an important process in their industries and it was very beneficial to apply US for decreasing viscous condition of polymer systems. Therefore, the advanced effect of US would be important in such industrial fields, but, such US effect on aqueous polysaccharides has not been known well yet. So, aqueous carrageenans and agar were used to study the US effect on the viscosity changes in aqueous solution. The US effect compared polysaccharides in their aqueous solution, κ and ι carrageenans and agar was measured, for this study using US at different frequencies of 23, 45 and 83 kHz.

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* Corresponding author. Tel.: +81 0258 47 9326; fax: +81 0258 47 9300.
E-mail address: takaomi@nagaokaut.ac.jp (K. Takaomi).

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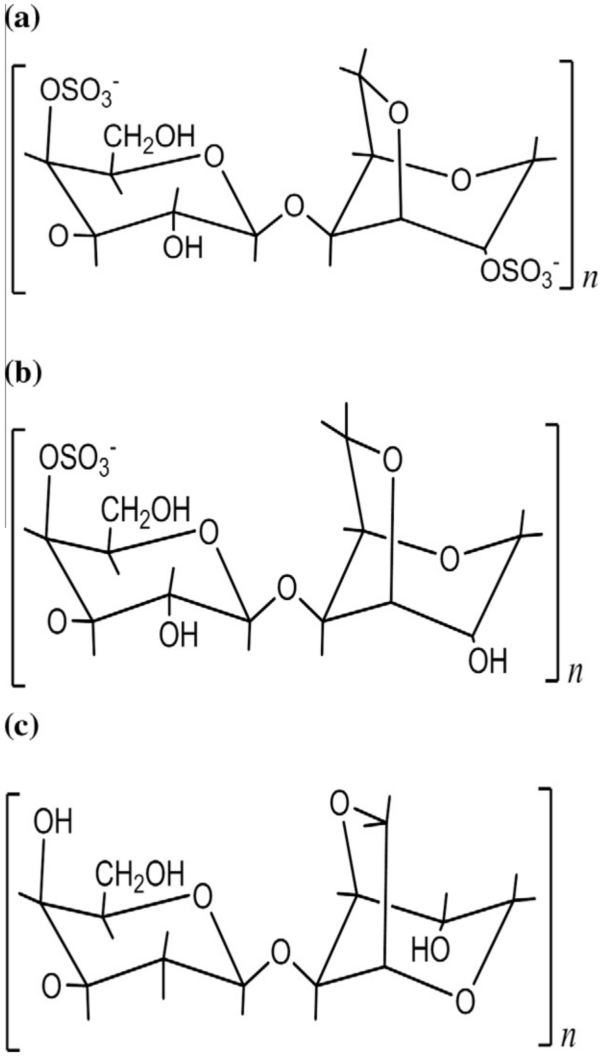

Scheme 1. Chemical structures of (a) ι-carrageenan, (b) κ-carrageenan and (c) agar.

2. Experimental

2.1. Materials

Polysaccharides such as κ-carrageenan and ι-carrageenan were purchased from TCI Co., Ltd. (Japan) and agar from Nacalai Tesque Co., Ltd. (Japan). All the chemicals were used without further purification. Each polysaccharide was used to prepare aqueous solutions dissolving in hot water at 80 °C and the powdered sample was continuously stirred by a magnetic stirrer. Aqueous solutions of κ-carrageenan, ι-carrageenan, and agar were prepared with 3 wt.% concentration in a glass vessel (diameter: 40 mm, height: 120 mm, and thickness of 0.14 mm) and used for the measurements of the shear viscosity. Water used to prepare solutions was distilled and purified using an ion exchange column.

2.2. Measurements of shear viscosity of aqueous polysaccharides

Fig. 1 shows the measure setup of ultrasonic bath (Ultrasonic Multi Cleaner W115, Honda Electronics Co., Ltd. 30 × 30 × 30cm^3) with seven piezoelectric pieces of 3 cm of diameter on the side wall. The bath was connected to a controller, which can produce different frequencies 28, 45 and 83 kHz with an input power in the range of 200–300 W.

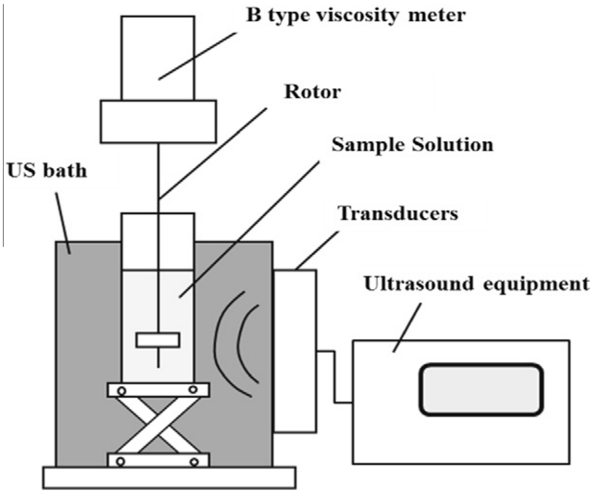

Fig. 1. Scheme of the experimental setting for the measurement of the shear viscosity in polysaccharides solutions with US exposure.

The temperature was measured with a Digital Thermo Hygrometer (Custom, CTH-1365) and controlled through whole experiments in the water bath by using a type immersion heater (Hakko, Japan). Then, the voltage was controlled with an alternate current voltage adjustment machine (Tokyo-Rikosha Co. Ltd., Slide Transform RSA RSC Series) was calibrate to give a temperature out of 60 °C in the submergible heater.

A calorimetric study was carried out to determine the dissipated power in the water bath [15]. The dissipate power of each frequency was controlled at 50 W in the water bath. All of the experiments were carried out at 60 °C in order to get a viscous aqueous solution. The shear viscosity was measured before and after the US operation by a Brookfield viscometer rotating cylinder (Tokyo Keiki Inc.). The sample vial containing the aqueous carrageenan or agar solution was set in the ultrasonic bath before the US irradiation for about an hour at 60 °C. The US exposure was carried out for 5 min and then, the US was turned off. After US was stopped, immediately the shear viscosity was measured with 1 min interval. Until, the value of the shear viscosity returned back to the original value. Sample solutions were similarly exposed to the US during 5 min each at frequency of 28, 45 and 83 kHz. The rotation of the Brookfield type viscometer was 60 rpm at 60 °C with rotor No 2. In order to confirm the US effect on the degradation of polysaccharides, HPLC profiles were measured and compared before and after the US exposure at different frequency. In the experiment, HPLC system (CCPS, Tosoh Corp), equipped with UV detector (UV 800, system Instruments Co., Ltd.) and TSKgel 5000 column was used. The polysaccharides profiles before and after the US exposure were obtained without change in the chromatograms. This indicated that no degradation of the polysaccharides was confirmed by the US exposure at 50 W for 5 min of exposure.

2.3. Determination of US effect on FT-IR spectra of the polysaccharide solutions

To determine chemical changes of the polysaccharides solutions, FT-IR spectra were measured on a JASCO FT-IR/4100 spectrometer using two CaF$_2$ plates with diameter 30 mm and thickness 2 mm (Pier Optics Co. Ltd.). As shown in the Scheme 2, on one side of the plate, a small amount of polysaccharide solution with 3 wt.% concentration was dropped. Then, the other plate was press to cover the dropped solution; thereby, a thin layer of the polysaccharide was produced between the two plates. In order to