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Physical properties of tofu gel probed by water translational/rotational dynamics

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ABSTRACT

The dynamic behavior of water molecules in tofu gels is observed using dielectric spectroscopy (DS) and pulsed field gradient nuclear magnetic resonance (PFG-NMR) methods. The breaking stress of tofu gels are dependent on the heating time, which affects the water structures characterized by the dielectric relaxation time, τ. On the other hand, the inhomogeneity of the gel structures decreases with increasing coagulant concentration was reflected as decreasing of the dielectric broadening parameter, β, that related for a fluctuation of the dynamic water structure. In addition, a decrease in the translational diffusion coefficient of water molecules is obtained with increasing coagulant concentration suggesting a reduction of the free space for the diffusional motion of water molecules. Negative correlations between the broadening parameter, β, and the inverse of diffusion coefficient, $1/D$, are found in tofu gels and soymilk with distinct correlation coefficients of −0.95 and −0.87, respectively. These results suggest that water dynamics analysis and complementary analysis using DS and PFG-NMR measuring techniques can be an effective tool to evaluate food gel physical properties. Further these technique could also explain the molecular mechanisms of gel and liquid structures and properties via dynamic water structures.

1. Introduction

Tofu, also known as soybean curd, is an ordinary gelatinous food with high water content that is traditionally eaten in Japan and several Asian countries. In recent years, tofu has been recognized as being healthy even in the Western countries because of its natural high protein and low fat content and because it is inferred that tofu reduces the development of some types of cancer (Messina, Persky, Setchell, & Barnes, 1994; Wu et al., 1996). The typical recipe for tofu involves heating soymilk with small amounts of coagulants, such as magnesium chloride or calcium chloride. Interestingly, tofu shows various textures depending on the coagulant concentration or type (Prabhakaran, Perera, & Valiyaveettil, 2006); heating time (Kohyama, Sano, & Doi, 1995); and amount of soybean protein (Cheng, Shimizu, & Kimura, 2005; Kohyama, Murata, Tani, Sano, Doi, 1995) which means that tofu is suitable for the food gel model due to its controllable property. In the field of food science, multiple papers have already reported on the gel structures of tofu (Nishinari, Fang, Guo, & Phillips, 2014), especially, those based on its mesoscopic/microscopic properties investigated via mechanical measurements (Cheng et al., 2005; Fuchigami & Teramoto, 1997; Huang & Kuo, 2015), ultrasound measurements (Kuo, Lien, Huang, & Ting, 2011), and scanning electronic microscope (SEM) or confocal laser scanning microscopy (CLSM) observations (DeMan, DeMan, & Gupta, 1986; Onodera, Tomotada, & Nakasato, 2009; Préstamo, Lesmes, Otero, & Arroyo, 2000; Urbonaite, De Jongh, Van Der Linden, & Pouvreau, 2015). According to these studies, the gelation model of tofu assumes, to a certain extent, that the soy protein aggregates, thus holding water in pores of tens to hundreds of micrometers (Kohyama et al., 1995a; Peng, Ren, & Guo, 2016). Experimental techniques, for example, nuclear magnetic resonance (NMR), dielectric spectroscopy (DS), FT-IR, and circular dichroism (Nagano, Akasaka, & Nishinari, 1995) provide information of molecular dynamics and structures through analyses of molecular behaviors, such as the molecular rotation, translation, and vibration. Specifically, reorientations and translations of water molecules respectively observed by DS and NMR methods could be complementarily analyzed with larger scale behaviors obtained from mechanical measurements (Li et al., 2014, 2015). Therefore, there is not a sufficient understanding of the dynamic structure of tofu gels on the molecular scale.

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As other aqueous gel systems, tofu gels contain large amounts of water, approximately 80%–90% (Wang, Swain, Kwolek, & Fehr, 1983). Therefore, the water content and the molecular interactions greatly affect the physical properties e.g. viscoelasticity of tofu gels. Nevertheless, it is extremely difficult to directly observe dynamic behaviors of water molecules because of remarkably fast dynamics of water molecules and the hydrogen-bonding networks with the characteristic time of 8 ps, in which the elementary process of molecular motions is rotations of water molecules. Although drying (Cai & Chang, 1997) or the centrifugation (Tang, Chen, & Foegeding, 2011) methods are often employed to determine the water content, dynamic behaviors of water molecules in tofu gel cannot be obtained from these methods.

For these reasons, a non-invasive and dynamic water observation technique is required to examine tofu in the food industry and to gain scientific understanding. Therefore, we used the pulsed field gradient NMR (PFG-NMR) method and dielectric spectroscopy (DS) to observe the translational and rotational water dynamics, respectively.

The PFG technique has been applied in various scientific research fields. In the earlier period of its development, the potential of the field gradient method drew a lot of attention due to its usefulness of nuclear spin system controllability. The first study to obtain a diffusion coefficient and expression was conducted by Stejskal and Tanner (Stejskal & Tanner, 1965) by using PFG spin echo sequence. In the field of medical science, the magnetic resonance imaging (MRI) with using the PFG method is indispensable in obtaining anatomical images for diagnoses. Currently, the PFG method is used as a general method of NMR to examine physical properties, and to develop strategies for medical diagnoses. In this study, we applied the PFG technique to obtain the water translational diffusion coefficient in the tens of milliseconds region.

The DS analysis is based on the dynamic behaviors of the permanent dipole moments of atomic groups or molecules under an alternating electric field. Multiple dielectric studies have been performed in the MHz-GHz frequency region for aqueous solution systems, e.g., polymer solutions, protein solutions (Shinyashiki et al., 2009), and solutions in food systems (Maruyama et al., 2014; Miura, Yagihara, & Mashimo, 2003). Based on the study of Li et al. (Li et al., 2014), there are three types of waters in tofu gels: water that exists freely, near the surface of proteins, and tightly bound with proteins. It is assumed that the latter two components of water appear in the less than MHz region (Abe et al., 2017; Mashimo, Kuwabara, Yagihara, & Higasi, 1987). Unfortunately, in the less than MHz region, there are vast contribution of the direct current (DC) component with the coagulant ions, which obstructs the relaxation process in certain regions. Therefore, we can only focus on the free water dynamics that usually appear in the GHz region with negligible DC components. The dielectric relaxation time of pure water, τ, is 8.27 ps at 25 °C (Kaatze, 1989), which indicates the characteristic time of the dynamics of the hydrogen-bonding network. This relaxation process provides valuable information concerning the dynamics of the water structures in aqueous systems and applies several analytical methods, such as a fractal analysis (Ryabov, Feldman, Shinyashiki, & Yagihara, 2002) to evaluate the distribution of water molecules in aqueous materials from the average and fluctuation of dynamic behaviors of water molecules (Yagihara et al., 2007).

In this study, we performed high-frequency DS and PFG-NMR measurements on tofu gels and soymilk to observe the rotational and translational water dynamics directly in the gels. We propose this method as a novel analysis method for food gels to characterize the viscoelastic property. Furthermore, the correlation between the dielectric relaxation and translational diffusion processes with respective time and length scales was considered to explain these molecular mechanisms in the water structures.

2. Experimental

2.1. Sample preparation

Tofu gels were made by mixing soymilk with a coagulant in a water bath at 80±0.1 °C. The concentrations of magnesium chloride hexahydrate (Wako 1st Grade, Wako Pure Chemical Industries, Osaka, Japan) used as the coagulant were set from 0.4 wt% to 0.7 wt %. The heating time was varied with values of 10 min, 30 min, and 60 min. After the heating procedure for the gelation process, each sample was stored during several minutes at room temperature to make it cool down before the measurements. Two types of soymilk samples were prepared: the first was commercial soymilk comprising a 9% soy protein component, and the second one was made from a soy protein isolate (SPI) dissolved in ultrapure water with various concentrations of 5 wt%, 7 wt%, and 9 wt%. As SPI sample, Fujipro F kindly supplied by Fuji Oil Co., Ltd. (Osaka, Japan) was used. The Fujipro F is composed of 21% 7S glycinin, 41% 11S glycinin, 38% other lipoprotein, and 1.5% cations. The solutions were heated at 100±0.1 °C in a water bath for 3 min before adding the coagulant for complete dissolution of the SPI. These preparation procedures were carried out based on a report by Cheng et al. (Cheng, Shimizu, & Kimura, 2004). The prepared sample conditions are listed in Table 1 for each heating times coagulant concentration, and SPI concentration.

The tofu samples were prepared in 5-ml vial tubes for the DS measurements. Bubbles were carefully removed via a pipette before heating to ensure a smooth contact of the electrode surface with the sample. Isolated water that appeared after the gelling processes was also removed before measurements. A glass capillary was used for the PFG-NMR measurements as described below with the same heating procedures. The sample amount required for DS and NMR measurements were around 3 ml and 100 μl, respectively.

Table 1
The three dielectric relaxation parameters, the dielectric relaxation time τ, the dielectric relaxation time broadening parameter β, the dielectric strength $\Delta\varepsilon$, and the diffusion coefficient D and the sample condition, the SPI concentration, coagulant concentration c, and heating time t, obtained by the series of experiments.

	SPI (wt%)	c (wt%)	t (min.)	τ (ps)	β	$\Delta\varepsilon$	D(m^2/sec)
Soymilk[a]	5	–	–	7.93	1.000	72.1	2.08×10^{-9}
	7	–	–	9.33	0.910	58.9	2.00×10^{-9}
	9	–	–	1.02	0.882	51.1	1.92×10^{-9}
Tofu Gel[a]	7	0.5	30	9.21	0.913	63.0	1.87×10^{-9}
	7	0.6	30	10.12	0.895	61.4	1.82×10^{-9}
	7	0.7	30	8.40	0.926	64.8	1.91×10^{-9}
	9	0.5	30	11.26	0.911	63.5	1.93×10^{-9}
	9	0.6	10	9.67	0.907	66.3	1.88×10^{-9}
	9	0.6	30	10.36	0.949	71.9	1.81×10^{-9}
	9	0.6	60	8.44	0.983	73.3	1.78×10^{-9}
	9	0.6	120	9.24	0.884	60.1	1.88×10^{-9}
	9	0.7	30	9.27	0.911	62.9	1.79×10^{-9}
Tofu Gel[b]	–	0.4	10	8.26	0.974	63.3	2.06×10^{-9}
	–	0.4	30	8.39	0.974	63.1	1.99×10^{-9}
	–	0.4	60	8.52	0.982	64.1	2.01×10^{-9}
	–	0.5	10	8.13	0.966	65.9	1.99×10^{-9}
	–	0.5	30	8.45	0.974	63.3	1.99×10^{-9}
	–	0.5	60	8.52	0.961	62.0	2.00×10^{-9}
	–	0.6	10	8.20	0.962	64.9	1.96×10^{-9}
	–	0.6	30	8.45	0.968	62.9	1.96×10^{-9}
	–	0.6	60	8.52	0.968	62.0	1.99×10^{-9}

[a] Made from a SPI dissolved in ultrapure water and measured by TDR.
[b] Made from commercial soymilk consisting of a 9% soy protein component and measured by VNA.