Fractal water structures affected by softener agent in cotton cloths

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ABSTRACT

Broadband dielectric spectroscopy (BDS) measurements were performed on cotton cloth samples with softener agents in natural environments, and a recent analytical technique of fractal analysis refined in dielectric spectroscopy was used for water structures. Three relaxation processes observed in the GHz, MHz, and kHz regions were attributed to the dynamic behaviors of hydrogen-bonding networks (HBNs) of water and interacting molecules, hydrated polymer chains, and ions restricted in the interfaces of large structures. Fractal analysis of the GHz region suggested that the GHz frequency process was retained, even in the dry state, revealing a broad spatial distribution of HBN fragments of various sizes. This typical tendency for heterogeneous hydration in cotton cloth was emphasized by the addition of a softener agent, as the value of Cole–Cole’s relaxation time distribution parameter changed from 0.55 to 0.41. The addition of the softener agent still retained the GHz frequency process, even in the dry state. This result means that the softener inhibited the formation of hydration sites on the cellulose surface and induced the dispersion of hydration sites. Thus, HBNs are fragmented by the softener agent. On the other hand, water molecules still aggregate to retain HBNs in a restricted area. The heterogeneous dispersion of HBN fragments broadens the GHz relaxation process, and the lower-frequency tail overlaps with the lower relaxation process because of chain dynamics with interacting water molecules. The structure formed by these water molecules, which is restricted by polymer chains and related to the stiffening effect of cotton fabric, is also heterogeneously hindered by the appropriate concentration of the softening agent. These indications were also consistent with the $T_2$ relaxation time obtained using the Carr–Purcell–Meiboom–Gill method of nuclear magnetic resonance measurements and are consequently reflected in the hydration model for macroscopic properties of cotton fabric.
Graphical Abstract

Introduction

Recently, many studies on the hydration structure of cotton and related materials have been published [1–11]. Experimental techniques to observe and analyze the dynamics of water molecules differ in wet or dry states. Moist materials, particularly in the dry state, typically have voids that trap water molecules and air, and heterogeneous structures present significant challenges for both measurement and analysis techniques. As fundamental knowledge, it is important to obtain the properties of cotton at various moisture levels; it is also crucial to evaluate the properties of cotton materials in our natural environment, where they are used in their natural dry state.

Dynamic behaviors of water molecules and interacting macromolecules and ions in hydrated structures of cotton cloth and threads for the naturally dry state have been recently reported using broadband dielectric spectroscopy (BDS) and nuclear magnetic resonance (NMR) measurements [5–11]. The hydrogen bonding network (HBN), consisting of water and interacting molecules, is fragmented into various sizes and spatially distributed in cotton materials [11]. Recent research on the dielectric properties of hydrogen-bonding materials suggests that the number density of hydrogen-bonding sites corresponds to mobility as the relaxation mechanism can be treated as a rate process of switching hydrogen bonds (HBs).
Considering recent interpretations of the GHz process, water structures in cotton materials with low water content are expected to be discussed from the aspect of fragmentation of HBNs, which cannot be analyzed easily using conventional methods [11, 15, 16]. Broad dynamic behaviors of water molecules have also been confirmed by $T_2$ analysis of NMR measurements [11].

An author (T. I.) investigated a hydration model of cotton cloth to explain the hardening effect of dry cotton rags prepared from the wet state [1–3]. The model shows that cotton stiffness is caused by a cross-linked network between single fibers mediated by capillary adhesion of bound water on the cellulose surface. The existence of bound water under naturally dried conditions has been implied through more straightforward information obtained from atomic force microscopy and atomic force microscopy – infrared spectroscopy [3]. The hydrogen-bonding state of the bound water distinct from that of the bulk water indicates a relationship between the microscopic nature of the bound water and the macroscopic mechanical behavior of cotton fabric [3, 4]. Our previous study [11] also suggested that the hydration structure of cotton cloth was characterized by the heterogeneity, implying a close relationship of the spatial distribution of water molecules with its physical properties. Fractal analysis of dielectric spectroscopy was effective in obtaining spatial distribution information of water structures. More examples of characteristic properties of cotton materials consistent with the hydration model above are desired.

In this study, BDS and $T_2$ relaxation of NMR measurements were performed on cotton cloth and yarn samples dried in natural environments. The relaxation parameters and spatial distribution of HBN fragments analyzed by recent fractal analyses of BDS and NMR spectra [11, 16] were discussed in terms of the effects of a softener agent governing water structures and molecular mechanisms.

Materials and methods

Preparation of cotton cloth samples

Plain-woven parts of cotton towels (TW220, Takei Corp., Japan) were used as samples. Before the experiment, these fibers were pre-washed completely using two methods (A and B) to remove all fiber-treatment agents used to manufacture the fibers. Next, these cotton cloth samples were purified with a mixed bed type of ion-exchange resins (501-X8, manufactured by Bio-Rad in the US) to remove ionic components, such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$, and K$^+$, from them. The resultant values of the elemental analysis were less than 10 mg/kg.

Method A: the samples were pre-washed using a fully automatic washing machine. Twenty-four cotton towels and 52.22 g of nonionic detergent (Emulgen108, Kao Corp., Japan, 10% aqueous solution) were put into a washing machine (NA-F702P, Panasonic Corp., Japan) with 47 L of water, and washed in two steps as follows: (1) the samples were washed for 9 min (with water containing the abovementioned nonionic detergent), rinsed twice with water, and sun-dried for 3 min. This step was repeated three times. (2) The samples were washed for 9 min (with water only), rinsed twice with water, and sun-dried for 3 min. This step was repeated twice.

Method B: the samples were pre-washed with organic solvents. Cotton towels were first divided into pieces (8 × 8 cm) and pre-washed using method A. Then, they were washed again while stirring in a beaker with 300 mL of CHCl$_3$/MeOH (1/1 wt ratio) for 5 min, and this process was repeated five times. Polyester faille and cotton yarn samples were washed only with solvent.

Softener treatment

Dioctadecyl dimethyl ammonium chloride (DODAC; Tokyo Kasei Corp., Japan) was used as the model softener, without purification. The concentration of the softener used to treat the thread and cloth was chosen according to the necessary testing conditions. Ion-exchanged water (400 mL) and 0.3% softener dispersion (the softener treatment concentration was set to 0.1% on the weight of fabric [o.w.f.]; (the standard concentration), and 1.0% o.w.f. (10 times of the standard concentration) were placed in a 500-mL beaker and stirred for 1 min. Three pieces of the abovementioned cloth were immersed in this aqueous solution and stirred for 5 min (the bath ratio was 100). The treated wet cloth samples were spread on a polypropylene sheet and allowed to dry naturally.

Thus, the samples obtained were kept in the laboratory at a constant temperature and relative
humidity (RH) of 23 ± 1 °C and 50 ± 1%, respectively, for several days before all measurements.

In this study, three types of cotton cloth samples were obtained: (1) untreated samples referred to as a blank; (2) 0.1% o.w.f. softener-treated samples with the agent; and (3) 1.0% o.w.f. softener-treated samples with the agent.

**Broadband dielectric relaxation measurements for cotton cloth samples**

High-frequency dielectric spectroscopy measurements were performed using the time-domain reflectometry (TDR) method [17–23] with a digitizing oscilloscope mainframe (54120B, Hewlett Packard) with a four-channel test set (HP 54124A) for dry samples in a frequency range of 100 MHz to 10 GHz. The electrodes used in this study were handmade open-ended coaxial electrodes with an outer conductor with an outer diameter of 2.2 mm [15, 16, 20, 24, 25]. After calibration, measurements were performed using ultrapure water (Milli-Q, Millipore) for wet samples and with 1, 4-dioxane for dry samples as the reference samples [19, 20]. The flat end of the semirigid coaxial electrode was set up to have good contact with the sample surface, and dielectric measurements were performed for each sample three times to confirm the reproducibility of the contact at 21 °C ± 1 °C and 50% ± 1% RH.

For dielectric measurements in low- and middle-frequency regions, an impedance analyzer (IA; 4294A, Agilent Technologies, 40 Hz–110 MHz) and an impedance/material analyzer (IMA; HP4291B, Hewlett Packard, 1 MHz–1.8 GHz) were used with handmade two-terminal parallel-plate electrodes inside the SMA-type connector [11, 26]. The C0 value was approximately 0.45 pF. Details of the dielectric relaxation measurements with the BDS measuring system [22, 27–30] for cotton cloth have been described in our previous study [11].

The water content was determined by mass measurements for each sample in the absolute dry state obtained from vacuum drying at 110 °C for 24 h after the dielectric measurements. The water content thus obtained for samples with 0, 0.1, and 1.0% o.w.f. softener concentrations was 5.0, 5.1, and 4.5 wt%, respectively. These water contents around 5 wt% are in good agreement with those reported in literature [10, 31–33].

**Nuclear magnetic resonance measurements for cotton yarn**

NMR measurements were performed using the 400-MHz NMR spectrometer (Ascend 400WB, Bruker) with a 5-mm-diameter NMR tube to obtain the $T_2$ relaxation time for cotton yarn samples. The Carr–Purcell–Meiboom–Gill (CPMG) method [34] was used to determine the $T_2$ relaxation time with 32 times integration. After obtaining the background signals, the difference between the background signals and the sample signals obtained for the sample inserted in the tube was analyzed.

The cotton yarn samples were maintained in a constant temperature and humidity chamber of 23 ± 2 °C and 50 ± 5% RH, respectively, for approximately 1 week in advance. To prepare the humidified samples, one end of the sample tube was cut and both ends were opened, and the sample tube was kept in a desiccator with 98% RH for 1 week. The tube was sealed again with silicon putty before NMR measurements. Results were obtained by averaging 3–8 samples under each condition. In addition, some samples were vacuum-dried at room temperature for approximately 1 week and then placed again in a chamber with a constant temperature and humidity to confirm reproducibility [11].

**Results and discussion**

**Relaxation parameter analysis of the GHz process**

Figure 1 displays the results from Yagihara et al. [11], showing the frequency dependence of the complex permittivity obtained from TDR measurements in the GHz frequency region for naturally dry cotton cloth samples, along with the result of lower-frequency measurements by IMA and IA measurements.

For TDR measurements, the average of three independent measurement results is represented by the black plots in Fig. 1 with the other three lower-frequency processes. Scattering data shown at 10 GHz frequencies was unavoidable despite the calibration because of the non-uniformity of the cotton cloth sample in the dry state with a small moisture content as discussed in our former paper [11]. The solid black line was obtained by fitting procedures for the entire relaxation curve with four Cole-
Cole-type relaxation functions [35] (dotted lines), as described in the following equation:

\[ \varepsilon^*(\omega) = \varepsilon'_\infty + \sum_{i=1}^{4} \frac{\Delta \varepsilon_i}{1 + (j\omega \tau_i)^{\beta_i}} + j \frac{\sigma_{DC}}{\varepsilon_0 \omega}, (0 \leq \beta_i \leq 1) \quad (1) \]

Here, the complex dielectric constant \( \varepsilon^* \) defined by \( (\varepsilon' - j\varepsilon'') \) is normalized by the relaxation strength, \( \Delta \varepsilon = \varepsilon'_\infty - \varepsilon'_1 \); \( \varepsilon'_1 \) and \( \varepsilon'_\infty \) are the low- and high-frequency limits of the dielectric constant, respectively. \( \omega \) represents the imaginary unit, \( \omega \) represents the angular frequency, \( \tau \) represents the relaxation time, \( \beta \) represents Cole–Cole’s symmetric relaxation time distribution parameter, \( \sigma_{DC} \) represents the DC conductivity, and \( \varepsilon_0 \) represents the permittivity of the vacuum. When \( \beta \) is unity, the relaxation process is described by the Debye equation [36]. The measurement methodology of dielectric spectroscopy and analytical techniques has been investigated for naturally dry cotton cloth samples [11]. The difficulty in measuring permittivity close to unity in the GHz region of heterogeneous materials with air voids is alleviated by estimating the entire relaxation curve with data in both high- and low-frequency regions. Analytical techniques can provide a more accurate assessment of relaxation processes in both high- and low-frequency regions. More detailed discussions for errors and fluctuations in these data are explained as recent analytical techniques previously [11].

According to previous results obtained for typical aqueous materials, three relaxation processes shown in Fig. 1 in the GHz, MHz, and kHz frequency regions were attributed to the dynamic behaviors of water molecules, hydrated polymer chains with bound water and ions, and ion behaviors restricted in the interfaces of large structures, respectively [11, 15]. The relaxation process shown in the frequency region of less than 100 Hz reflects electrode polarization. Thus, the relaxation parameters obtained for the GHz process by fitting procedures are listed in Table 1.

Figure 2 shows dielectric relaxation curves obtained for cotton cloth samples with the softener agents with concentrations of (a) 0.1% and (b) 1.0% o.w.f. Experimental data plots in Figs. 1 and 2 show large deviations from the relaxation curves. These deviations can be caused by the contact between electrodes and the sample surface, porosity of materials, nonuniform hydration, etc. However, suitable curves could be obtained to fit the entire experimental data in the respective frequency regions.

Table 1 shows small \( \beta \) values for the GHz process [15]. The broad relaxation curves shown in Figs. 1 and 2 indicate that the kHz and MHz processes were also broad, similar to those obtained in the solid or glassy state. This result also explained the reason why the relaxation strength and relaxation time cannot be determined easily by the fitting procedures, and the difficulty in the procedure is a characteristic feature of the dry cotton samples. In addition, although it is impossible to have permittivity less than unity, it is, generally, difficult to determine the exact value of \( \varepsilon'_\infty \) at the high-frequency limit, and deviations of up to 2 and 3 can easily cause an offset for permittivity. As discussed in our previous study [11], the difficulty and tendency were also shown for the relaxation time, 3 ps, which is less than 8 ps typically obtained for bulk water. Broadening in the GHz frequency process without a clear loss peak in the frequency region of observations is thought to easily affect fitting procedures and tends to offer smaller values of the relaxation time. However, we did not use any restrictions for the relaxation
parameters used in the fitting procedures to avoid further induction of artificial error [11].

To investigate the ambiguities in the fitting procedures, values of the relaxation strength, $\Delta_e$, and the relaxation time distribution parameter, $\beta$, were obtained for all samples and are shown in Figs. 3 and 4, respectively. In most fitting procedures, relaxation strength greater than the correct values results in a smaller relaxation time distribution parameter. However, relaxation parameters obtained for these samples show the same increase or decrease tendency in Figs. 3 and 4. Therefore, this study’s result of the relaxation parameters was not obtained using simple artificial errors of fitting procedures. Furthermore, another confirmation was investigated with the fixed peak frequency at around 10 GHz. Though the determination of the peak frequency of the GHz process indicates a tradeoff relationship with the relaxation strength, the same tendencies of the relaxation parameters obtained for all samples were confirmed. These confirmations mean that the relative relaxation parameters were sufficiently reliable, even if each absolute value has errors.

The water content estimated from the relaxation strength for the GHz process shown in Table 1 is 1.7, 1.5, and 1.8 wt% for samples with the softener concentration 0, 0.1 and 1.0% o.w.f., respectively. These values are smaller than those obtained by mass measurements for the water content, 5.0 ± 0.3, 5.1 ± 0.2, and 4.5 ± 1.4 wt%, respectively. Due to the difficulty in observing and analyzing the wide distribution of restricted water molecules and sometimes the presence of air in dry cotton samples, dry cotton samples usually show lower values of the

Table 1 Values of relaxation parameters of the GHz process obtained by three independent TDR measurements at the laboratory temperature of 21 °C for naturally dried cotton cloth samples

| Cotton cloth samples                        | measurements | $\tau$/ps | $\Delta_e$ | $\beta$ |
|--------------------------------------------|-------------|-----------|------------|--------|
| Natural dry sample without softner agent   | 1st         | 3.0       | 1.23       | 0.55   |
|                                            | 2nd         | 3.0       | 1.29       | 0.55   |
|                                            | 3rd         | 3.0       | 1.29       | 0.55   |
|                                            | Average     | 3.0       | 1.27       | 0.55   |
| Natural dry sample with 0.1% softner agent | 1st         | 1.8       | 1.11       | 0.41   |
|                                            | 2nd         | 1.9       | 1.11       | 0.41   |
|                                            | 3rd         | 2.1       | 1.12       | 0.41   |
|                                            | Average     | 1.9       | 1.11       | 0.41   |
| Natural dry sample with 1.0% softner agent | 1st         | 8.9       | 1.32       | 0.61   |
|                                            | 2nd         | 7.1       | 1.32       | 0.61   |
|                                            | 3rd         | 8.1       | 1.32       | 0.61   |
|                                            | Average     | 8.0       | 1.32       | 0.61   |

Figure 2 The BDS spectrum obtained from three subsystems in respective frequency regions for dry cotton cloth samples with an average TDR measurement data for samples with treatments of a 0.1% o.w.f. and b 1.0% o.w.f. softener agent.
apparent water content. These explanations also reported in our previous paper [11] are generally available in dynamics observation methods such as NMR measurements. Broader NMR spectra are observed for lower water content samples [31].

Relaxation parameter analysis of BDS spectra

In conventional analyses of the GHz process of dielectric spectroscopy for aqueous complex systems, there exists an analytical technique, where the dielectric relaxation curve is fitted by superpositioning multiple Debye-type single relaxation functions. However, compared with the results of broadband dielectric measurements, (1) the tail of the relaxation curve extending from the neighboring frequency range cannot be eliminated and (2) detailed fitting procedures with multiple Debye functions easily produce, for example, a 20-dimensional error space that exceeds 20 parameters when separated more finely. Although it is a judgment, as a further increase in experimental conditions complicates the interpretation, this analysis uses three processes of GHz, MHz, and kHz. For example, a model has been reported in which the MHz process is further separated into multiple bound waters [10]. In this study, we decided to use an analysis method representing the minimum required relaxation process.

In the fitting procedure of the relaxation curve obtained from BDS measurements using some model functions, how many relaxation processes are assumed is important. On the other hand, especially in the case of complex systems, not only the number of relaxation processes but also how to express the distribution of the relaxation time for each process is critical. It is insufficient to characterize structures and physical properties of complex systems with their average values, and introducing the concept of fluctuations leads to their final characterization. Then, the evaluation of fluctuations is the most important factor in the analysis and interpretation of complex systems with a dynamic hierarchical structure. In the conventional analysis of the GHz frequency process observed by dielectric spectroscopy for aqueous complex systems, the superposition of multiple Debye-type single relaxation functions is performed frequently.

The BDS measurement results in Figs. 1 and 2 show that the tails of relaxation curves extending from the neighboring frequency process widely overlap, and a lot of Debye-type relaxation processes were required for the fitting procedure, especially for such heterogeneous low-loss materials. In the fitting procedures, it is difficult to determine appropriate average values of the relaxation parameters for each process. Therefore, in this work, considering the entire relaxation curves obtained by BDS measurements, a GHz process reflecting HBN dynamics, an MHz process due to the restricted local motion of water, ions, and polymer chains overlapping with the...
lower-frequency tail of the GHz process, a kHz process reflecting the interface polarization due to molecules and ions restricted in large-scale structural boundaries, and the electrode polarization are assumed in fitting procedures.

Compared with a model [10], for example, in which the relaxation curve in the MHz frequency region is explained by multiple processes corresponding to respective bound waters with different interactions, this study requires a simpler and more comprehensive hydration model. Therefore, the relaxation time distribution parameters for respective relaxation processes are important in this study’s model to describe the relaxation curve using the minimum number of relaxation processes. In addition, it is suitable for the fractal analysis to characterize dynamic behaviors of HBNs, as described in the next section. To describe and interpret the structures and physical properties of aqueous complex systems, characterization based on the average value of physical properties, such as the relaxation time, is insufficient, and characterization based on the concept of fluctuation behavior is significantly more important. Treating fluctuations in dynamics as the most important factor for aqueous complex systems with a hierarchical structure shows an essential difference from conventional analyses.

Table 2 shows relaxation parameters obtained from the present fitting procedures for each relaxation process, including the GHz process. Though the relative differences among relaxation parameters of the various processes for each cotton sample with the softener agent are similar to those obtained for the sample without softener reported in our previous paper [11], some characteristic differences are shown. Typical errors of small $\tau$ and $\varepsilon_\infty$ values often found in high frequency measurements and analyses can be calibrated under artificial assumptions in fitting procedures. However, since the present study emphasizes the spatial distribution of water structures, which are implied from $\beta$ values determined from the frequency dependence of complex dielectric constant in the middle- and high-frequency regions [11], any artificial assumptions for $\tau$ and $\varepsilon_\infty$ values were not employed in the present work. All relaxation parameters obtained are summarized for respective processes and samples as bar graphs in Figs. 5, 6, 7. Figures 5 and 6 show larger relaxation strength values and larger relaxation times for electrode polarization than other relaxation processes, even if the relaxation strength are smaller than those typically reported so far for aqueous systems with larger water contents. A recent study on interface polarization for water/oil systems suggested that relaxation strength and time values depend on the length scale of heterogeneous structures because the length and time scales of ion migration depend on the structures [37]. On the other hand, the relaxation

| Cotton cloth samples | Various process | $\tau$ | $\Delta \varepsilon$ | $\beta$ |
|----------------------|----------------|-------|-----------------|-------|
| Natural dry sample without softener | Electrode polarization | 3.9 ms | 3.8 | 0.85 |
|                       | kHz process | 20 ms | 0.27 | 0.56 |
|                       | MHz process | 5.5 ns | 0.13 | 0.50 |
|                       | GHz process | 3.0 ps | 1.27 | 0.55 |
|                       | $\varepsilon_\infty$ | 0.02 | |
|                       | DC conductivity | 3.2 pS/m | |
| Natural dry sample with 0.1% softener | Electrode polarization | 6.0 ms | 4.0 | 0.89 |
|                       | kHz process | 35 ms | 0.25 | 0.56 |
|                       | MHz process | 16 ns | 0.11 | 0.50 |
|                       | GHz process | 1.9 ps | 1.11 | 0.41 |
|                       | $\varepsilon_\infty$ | 0.14 | |
|                       | DC conductivity | 3.2 pS/m | |
| Natural dry sample with 1.0% softener | Electrode polarization | 6.0 ms | 4.0 | 0.89 |
|                       | kHz process | 32 ms | 0.23 | 0.45 |
|                       | MHz process | 12 ns | 0.13 | 0.41 |
|                       | GHz process | 8.0 ps | 1.32 | 0.61 |
|                       | $\varepsilon_\infty$ | 0 | |
|                       | DC conductivity | 3.2 pS/m | |
strength for the kHz process seems less than that reported so far in the literature because of the lower water content. The relaxation time distribution parameters for GHz, MHz, and kHz processes are approximately 0.5, as shown in Fig. 7. These smaller values mean that the broad relaxation curves are overlapped, and the decomposition procedures of each process are essentially difficult.

Table 3 summarizes the changes in the relaxation parameters with additions of the softener agent for each process. The most important changes in the relaxation parameters are indicated by red arrows for the relaxation time distribution parameters rather than the relaxation strength and the relaxation time for which large errors and variations cannot be avoided. Although conventional analysis generally shows that the smaller relaxation time distribution parameters, the greater variation in the dynamic behavior of the water structure, a more detailed discussion on the relaxation time distribution parameters with fractal analysis is described in the following section.

**BDS and NMR analyses for hydration structure model**

The $\tau$-$\beta$ diagram first examined by Shinyashiki et al. [38] has been theoretically explained by Ryabov et al. [39, 40] and developed with more details by a three-dimensional diagram by Feldmann's group [41–44]. The $\tau$-$\beta$ diagram was also used as an analytical tool to characterize the spatial distribution of HBNs of water and interacting molecules in various aqueous systems, such as foodstuff [45–47] and cement.
materials [48], compared with a database, as shown in Fig. 8. Details on the physical meanings of the diagram have been discussed in our previous study [15, 16].

Plots obtained for cotton cloth samples are shown in Fig. 8. $\beta$ values obtained for cotton cloth samples with 0, 0.1%, and 1.0% o.w.f. softener agent were 0.55, 0.41, and 0.61, as plotted in Fig. 8, respectively. Not only are the $\beta$ values relevant in the fractal analysis but also combinations with the relaxation time, as explained in our previous reports with a detailed discussion [11, 16]. The characteristic feature of the GHz process obtained here is the retention of high-frequency components with small $\beta$ values, and this tendency becomes more pronounced for cotton cloth samples with the treatment of the softener agent. This result suggests that the HBN is fragmented and dispersed with the softener agent and water molecules [66, 67] even in single fibers [2, 6, 68] of cotton materials. Corrente et al. recently pointed out that the softener agent provides accessible volume for water molecules interacting with cellulose chains in amorphous regions contributing to the increase of the hygroscopicity of the fiber [69]. More water molecules interacting with cellulose chains exist on the surface of microfibrils [70, 71]. These hydrated cellulose chains with cooperative interactions with water molecules and ions are reflected in MHz process. The $\Delta \varepsilon$ value of the MHz process for the cotton sample with 0.1% o.w.f. softener agent is almost same with that of the sample without softener as shown in Table 3. This result means that the ratio to these values in the GHz process tended to increase by the addition of 0.1% o.w.f. softener agent. Considering that the relaxation strength of MHz process is affected by the amount of water molecules interacting with the chains, it implies that the fabric softener agent with the standard concentration increases the proportion of water molecules interacting with the cellulose around the microfibrils. These results suggest that the softener agent improves macroscopic and mechanical properties of cotton fabric with not only the surface interactions on the single fibers but also microscopic water structures inside the single fiber. The large HBN fragments should be remaining dynamic behaviors of bulk water; however, fragments with smaller sizes are also included to show a broad relaxation curve in the lower-frequency side. Smaller HBN fragments with small average values of the number density of hydrogen-bonding sites are continuously distributed, and except for decompositions by fitting procedures of the relaxation curve obtained by BDS measurements, we cannot distinguish the two contributions to the GHz and MHz processes.

A decrease in the $\beta$ value of the cotton cloth samples treated with 0.1% o.w.f. softener agent means a heterogeneous distribution of HBN fragments by the softener, and a re-entrant behavior of an increase in the $\beta$ value obtained for the sample with 1.0% o.w.f. softener concentration was observed. In the previous research [2], it was reported that softener cloth

| Relaxation process | Lowest freq | kHz process | MHz process | GHz process |
|--------------------|-------------|-------------|-------------|-------------|
| Information        | Electrode polarization | Interfacial polarization | Chain & water dynamics | HBN dynamics |
|                    | Conductivity | Ion dynamics | Chain mobility | Heterogeneity |

$\tau \rightarrow 0.1\%$ softener agent

| $\tau$ | $\Delta \varepsilon$ | $\beta$ |
|--------|---------------------|---------|
| $\nearrow$ | $\nearrow$ | $\nearrow$ |

$0.1\% \rightarrow 1.0\%$ softener agent

| $\tau$ | $\Delta \varepsilon$ | $\beta$ |
|--------|---------------------|---------|
| $\nearrow$ | $\nearrow$ | $\downarrow$ |

†, increase; ↓, no change; ‡, decrease; †, small increase; ‡, small decrease. Upward and downward rows indicate significant changes discussed in detail.
samples treated with 0.1% o.w.f. have characteristic uneven adsorption conditions, enabling us to link its high bouncy feeling. In case an excess amount of softener (1.0% o.w.f.) is used, uneven adsorption condition decreases, whereas the equality of adsorption condition improves. This characteristic result is phenomenologically explained as the excess amount of the 1.0% softener agent covers many more hydrogen-bonding sites on the surface of the cellulose microfibers, where water molecules are aggregated in HBNs [11, 16], than the 0.1% agent, thereby reducing the distribution of HBN fragments. The aggregation behavior of the softener and water molecules according to the concentration has also been reported in a surfactant deposition study by Oikomomou et al. [72]. Excess softener agents form large-scale aggregates with water around microfibrils, as indicated by the larger $\beta$ values, reducing the proportion of water molecules in HBN fragmentation. The minimum $\beta$ value suggests these aggregation structures of water and softener agent molecules. These aggregation structures of excess softener agents with water molecules are also suggested from the ratio of $D_e$ value for the MHz process against that for the GHz process, which does not increase with the softener agent concentration from 0.1 to 1.0% as shown in Table 3. The characteristic behavior of cotton samples with excess softener agent reflects the

Figure 8 $\tau$–$\beta$ diagram obtained for various aqueous systems and a plot obtained for the dried cotton cloth samples. The $\tau$–$\beta$ diagram obtained for various aqueous systems and a plot obtained for naturally dry cotton cloth samples. The various substances used for aqueous mixtures shown in the figure follow commonly used abbreviations, such as poly(vinylpyrrolidone) (PVP) [38], poly(ethylene glycol) (PEG) [38], poly(vinyl methyl ether) (PVME) [38], poly(ethylenimine) (PEI) [38], poly(acrylic acid) (PAA) [38], poly(allylamine) (PAA) [38], poly(N-isopropylacrylamide) (PNiPAM) [49], poly(acrylamide) (PAAm) [50], PAAm gels in water–acetone mixtures (PAAm gel acetone) [50, 51], PAAm gels in water–dimethyl sulfoxide mixtures (PAAm gel DMSO) [51], PAAm gels in water-1, 4-dioxane (PAAm gel 1, 4-dioxane) [51], trehalose [52, 53], maltose [52, 53], pullulan [54], glucose [52, 53], rice [46], hydroxypropylmethylcellulose (HPMC) [53, 55, 56], 1,2-dipalmitoylsn-glycero-3-phosphocholine (liposome) [53, 57–59], denatured chicken egg white (glass egg) [53, 60], ovalbumin (OVA) [53, 61–64], gelatin [53, 64], and bovine Achilles tendon (collagen) [52, 64, 65]. The plots obtained from the analysis of the GHz processes for naturally dry cotton cloth samples are shown as no treatment (Black Circle), 0.1% o.w.f. softener agent (Red Triangle), and 1.0% o.w.f. softer agent (Blue Triangle). The arrows indicate the maximum errors estimated from the $\tau$ value.
properties of the two-component system of softener agent and water. However, detailed properties of the two-component system, such as the phase transitions [59, 73] and the fluctuation in surrounding water structures [59] are affected by cellulose and air in dry cotton samples. Therefore, it is effective and essential to use complementary techniques such as FTIR [73] and NMR [11] with BDS.

On the other hand, the increase in bounce feeling determined from the sensory test with increasing concentration of the softener agent showed saturation behaviors with the excess softener agent above 0.1% o.w.f. [2]. Therefore, it is quite reasonable to consider that these macroscopic properties reflect water molecules interacting with cellulose molecules via HBs. The micro–macro relationship between molecular behaviors of the hydration structures and the mechanical properties of cotton cloth also suggests that the minimum $\beta$ value concentration provides an indication of the optimum fabric softener concentration, which is usually treated as 0.1% o.w.f. (the standard concentration).

It was reported that those broad distributions of dynamic behaviors of water structures according to the BDS measurement results were also consistent with the results obtained by the $T_2$ relaxation time analysis of NMR measurements for cotton yarn [11]. Figure 9 shows an example of the echo time dependence of the intensity background signal obtained using the CPMG method of NMR measurements for an empty NMR tube, the signal from a tube containing a naturally dry sample, and a subtracted signal of them. The decay observed for intensity was described by at least two exponential behaviors, even if the background signal was subtracted. Therefore, the signal $M(t)$ at echo time $t$ was described by following bi-exponential expression for the fast and slow decay processes, which are, respectively, characterized by the $T_{2f}$ and $T_{2s}$ relaxation times, as shown below

$$M(t) = A_f \exp\left(-\frac{t}{T_{2f}}\right) + A_s \exp\left(-\frac{t}{T_{2s}}\right)$$

(2)

Here, $A_f$ and $A_s$ are constants determining the intensity for the fast and slow processes. The $T_{2s}$ relaxation time reflects a component of water molecules with higher mobility than $T_{2f}$. The $T_2$ relaxation time was obtained from the slope of the straight line in Fig. 9.

Figure 10 shows a characteristic tendency of the concentration dependence of $T_{2s}$ and $T_{2f}$ relaxation times obtained for naturally dry samples of cotton yarn. The $T_{2s}$ value for the slow component with higher mobility was approximately 10 ms, and that for the fast component $T_{2f}$ with lower mobility was approximately 1 ms. The $T_{2s}$ value shows an increase of 35.7%, whereas the $T_{2f}$ value decreased by 10.8% for the sample with treatments of 1.0% o.w.f. softener agent compared with those for samples with no softener. This result suggests that the treatment with the softener increased mobility for the component with higher mobility and decreased mobility for the component with lower mobility. In other words, the fabric softener is supposed to emphasize the difference between the higher and lower mobilities of water molecules in the cotton yarn. These changes were not significant, as expected from the linear dependence on the softener agent concentration for samples with 1.0% o.w.f. softener, as shown by the deviations of plots from the lines in Fig. 10. Therefore, the effect of softener agent addition is expected to be remarkable for the sample with 0.1% o.w.f. softener agent treatment (standard concentration), and the effect seems saturated for the sample with 1.0% o.w.f. softener agent treatment. This tendency corresponds to the results obtained by the fractal analysis of relaxation parameters, and the coincidence should be reflected in the hydration model.

Figure 9 An example of the echo time dependence of the intensity background signal of the intensity obtained by the CPMG method of NMR measurements for an empty NMR tube (Black Circle), the signal from a tube containing a naturally dry sample (Red Triangle), and the subtracted signal of them (Blue Triangle). The red line was obtained from the fitting procedure with Eq. 2.
From the intensities, $A_f$ and $A_{sw}$ defined by Eq. 2, the change in the proportion of water content affected by softener agent addition was calculated. The results shown in Fig. 11 indicate that more than 90% of water molecules are included in the fast process with restricted dynamics, and softener agent addition increases the restriction. It is reasonable to consider that almost all water molecules are restricted in dry samples. Furthermore, the increase and decrease in the amount of water restricted and mobile water molecules affected by the softener agent correspond to the remarkable changes obtained for the $T_2$ values. The tendency of saturation in the softener concentration dependency is also recognized in Fig. 11. These saturation behaviors also support characteristic features of the water structures obtained from dielectric properties.

On the other hand, even though meaningful analysis is expected for heterogeneous diffusion phenomena of water molecules observed by NMR measurements, sufficient strength could not be obtained for naturally dry samples because $T_2$ values are less than the diffusion time. Typically, in conventional NMR analyses, the discussion of fluctuations of dynamic behaviors has not always progressed. The elementary processes of dynamics, which are much shorter than the observation time scale and are averaged over a large observation time window, must be due to an observation problem [15, 16, 45, 47].

The $\tau$-$\beta$ diagram of a naturally dry cotton cloth sample shows characteristics similar to a heterogeneous system with a broad spatial distribution while maintaining the relaxation frequency range, rather than a low-frequency shift of the relaxation frequency range. Therefore, water structures in cotton cloth samples are characterized as follows: (1) even if the average water content is small, water molecules locally aggregate to form an HBN to retain the relaxation process in the GHz frequency region and (2) the HBN cannot penetrate the cellulose microfibrils with 4-nm diameter [9, 11]. This work further shows how the softener agent affects the dynamic behaviors of water molecules in cotton cloth samples and well explains that the concentration-dependent saturation behavior demonstrated by BDS and NMR measurements corresponds to each other. These considerations regarding the saturation behavior shown by dielectric and NMR spectroscopy suggest that the three softener concentrations, no addition, standard concentration (0.1% o.w.f.), and excess concentration (1% o.w.f.) provide the most effective water structure analysis. It is reasonable to consider that a simple softener concentration dependency of water structures cannot be obtained in an excess concentration region of softener agent.

According to the cotton hydration model proposed by Igarashi et al. [1–3], water molecules are not
removed uniformly during the natural drying process, leaving local HBN fragments on the 1-nm scale. Water molecules included in the HBN fragments contribute to the mechanical strength of cotton cloth samples. As a result of the mechanical stimulation, water molecules released from the HBN fragments contributed to the mechanical strength of cotton cloth samples and moved to the vicinity of cellulose molecules. These water molecules are restricted by the low HB site number density, and the lower-frequency tail of the GHz process is emphasized. Water molecules that contribute to the mechanical strength of cotton cloth samples are removed by further drying procedures. The softener agent is thought to reduce the local HBN fragments, covering the surface of microfibrils for the aggregation of water molecules. There is no contradiction between the explanation of the molecular mechanism based on the results obtained in this study and the cotton hardening model [1–3].

Conclusions

The fractal analysis of the GHz frequency process observed for cotton cloth suggested that HBN dynamics of water and interacting molecules heterogeneously were preserved, even in the dry state. This typical tendency of heterogeneous systems was emphasized by the addition of the softener agent, as the value of Cole–Cole’s relaxation time distribution parameter was changed from 0.55 to 0.41. The addition of the softener agent also retains the GHz frequency process, even in the dry state with the broadening of the spatial distribution of HBN fragments with various sizes. This result means that the 0.1% o.w.f. softener agent inhibited the formation of hydration sites on the surface of cellulose microfibers, where water molecules aggregated with interacting molecules in HBN fragments with various sizes, and induced dispersions of hydration sites. On the other hand, water molecules still aggregate to preserve the HBN in the restricted area. The spatial dispersion of HBN fragments broadens the GHz relaxation process, and the lower-frequency tail is overlapped with the MHz relaxation process for chain dynamics with bound water. The softening agent also interferes with the formation of HBN fragment, which is related to the stiffening effect of cotton fabric. Excess softener agents form large aggregates with water around microfibrils, reducing the proportion of smaller HBN fragments to larger $\beta$ values. Fundamental understanding of molecular mechanism thus obtained for water structures in cotton cloths and micro–macro relationships between molecular behaviors of the hydration structure and mechanical properties should be applicable for extensive and practical use of cotton fabric.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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