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Cellulose gels produced in room temperature ionic liquids by ionizing radiation

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Abstract

Cellulose-based gels were produced in room temperature ionic liquids (RTILs) by ionizing radiation. Cellulose was dissolved at the initial concentration of 20 wt.% in 1-ethyl-3-methylimidazolium (EMI)-acetate or *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium (DEMA)-formate with a water content of 18 wt.%, and irradiated with γ-rays under aerated condition to produce new cellulose gels. The gel fractions of the cellulose gels obtained in EMI-acetate and DEMA-formate at a dose of 10 kGy were 13 % and 19 %, respectively. The formation of gel fractions was found to depend on the initial concentration of cellulose, water content, and irradiation temperature. The obtained gel readily absorbed water, methanol, ethanol, dichloromethane, *N*, *N*-dimethylacetamide, and RTILs.

Highlight

- Cellulose gels were produced in room temperature ionic liquids (RTILs).
- Water plays a crucial role in the cross-linking reaction.
- Cellulose gels swollen with RTILs show good electronic conductivity (3.0 mS·cm^{-1}).

Keywords

cellulose, gel, room temperature ionic liquid, ionizing radiation.

1. Introduction

In recent years, natural polymers have attracted significant attention as alternative green materials because of the exhaustion of petroleum and non-renewable resources, and the increase in environmental pollution. Polysaccharides such as cellulose, chitin/chitosan, starch, and alginic acid are natural polymers. Large quantities of polysaccharide-based biomass are ubiquitous on Earth. They possess unique structures, distinctive properties, and offer the advantages of being non-toxic and biodegradable. They are often modified to produce functional materials, such as viscose rayon, personal care products, and biodegradable plastics. Ionizing radiation is widely used as a convenient tool for the modification of polysaccharides via decomposition, grafting, and cross-linking (Seko et al., 2005). Besides, chemically modified polysaccharides such as carboxymethyl cellulose, hydroxypropylmethyl cellulose, carboxymethyl chitin/chitosan, and carboxymethyl starch, all of which dissolve in water at high concentrations, have also been irradiated with ionizing radiation to obtain derivative gels that are used as materials for making water absorbents and wound dressings (Fei et al., 2000; Wach et al., 2001; Zhao et al., 2003; Zhao et al., 2008; Nagasawa et al., 2004; Pekel et al., 2004; Wang et al., 2007). Until now, radiation cross-linked materials have only been produced either from polysaccharide derivatives or using cross-linking reagents, as certain natural polysaccharides have poor solubility in water and organic solvents as well as low chemical reactivity (Kumar, 2000). These limitations could possibly be circumvented by the use of organic solutions that have high proton-accepting ability, such as chloroform in dimethylsulfoxide, *N*-methylmorpholine-*N*-oxide, lithium chloride (LiCl) in *N*,*N*-dimethylacetamide, calcium chloride in methanol, and room temperature ionic liquids (RTILs), which can cleave the hydrogen bonds of the polysaccharides to form solutions in the concentration range of 0.1–20 wt.% (Swatloski et al., 2002; Heinze et al., 2005; Fukaya et al., 2008).

Among these organic solutions, RTILs have attracted much attention in the diverse fields of chemistry, biology, engineering, and environmental science because of their unique functionalities such as specific solubility, chemical and thermal stabilities, unusual dynamical properties linked to high viscosity, and wide potential windows (Rogers, 2003). So far, several studies have been reported in the fields of photo- and radiation chemistry to identify more effective reactions between the charged reactive species in RTILs (Wishart et al., 2003; Wishart et al., 2005; Kondoh et al., 2009; Katoh et al., 2009; Kimura et al., 2010). In addition, extensive fundamental and applied research have been conducted on RTILs used in various fields such as radiation-induced polymerization (Qi et al., 2008) and radiation-induced grafting polymerization (Hao et al., 2009). However, to the best of our knowledge, there are no studies reported so far on the use of RTILs in radiation cross-linking reactions.

Therefore, in this study, we focus on the application of RTILs as “specific solvents for the dissolution of polysaccharides,” and their use in establishing a “proper reaction field for radiation cross-linking.” We propose a new method for the radiation modification of polysaccharides using RTILs to produce new functional and sustainable materials. Cellulose was selected as the polysaccharide of choice as it is the most prevalent plant-derived polysaccharide, which comprises the main component of plant plasma membranes and fibrous raw materials such as paper, wood material, and cotton. Recently, it has been reported that the degree of polymerization of 5 wt.% cellulose dissolved in 1-butyl-3-methylimidazolium (BMI) –chloride tends to reduce as a function of dose (Hao et al. 2012). Meanwhile, the scission reaction is preferred over the cross-linking reaction when the concentration of polysaccharide in the organic solvent is less than approximately 10 wt.% (Tabata et al., 1991; Nagasawa et al., 2004). We assume that cross-linked materials could be produced from cellulose via ionizing radiation in RTILs, which are capable of dissolving more than 10 wt.% of cellulose.

We designed and synthesized some RTILs as the reaction medium, in which cellulose could be dissolved to concentrations in excess of 10 wt.%, and further investigated the radiation-induced cross-linking of cellulose in each RTIL. The outcome of this study is expected to provide insights on new ways of functionalizing materials, including cellulose and other natural polymers.

2. Experimental

2.1 Sample preparation

Cellulose powder (Microcrystalline grade, Merck) was used as received and its viscosity-average molecular weight was estimated by the following Mark–Kuhn–Houwink–Sakurada equation:

$$[\eta] = K\ M_v^{\alpha} \tag{1}$$

where $[\eta]$ and M_v are the viscosity and viscosity-average molecular weight of the sample solution, respectively, and K and α are constants reported as 1.278×10^{-4} $cm^3 \cdot g^{-1}$ and 1.19, respectively (McCormick, 1985). In the typical process, pre-determined quantity of cellulose was dissolved in the solution of 9 wt.% LiCl (Wako, 98 %) in *N*, *N*-dimethylacetamide (DMAc, Wako, 97 %). The viscosity of the cellulose solutions in the concentration range 1 - 4 $g \cdot L^{-1}$ was measured using Ostwald and oscillatory viscometers (CBC Co., Ltd., Viscomate VM-10A). The weight-average molecular weight of cellulose was analyzed using a high-performance liquid chromatograph (HPLC, Shimadzu, SCL-10A) with gel permeation chromatography (GPC) columns (TSL-GEL ALPHA and 2500, Tosoh) and a refractive index detector (RI 704, GL Science). For HPLC measurement, the flow rate of the 30 mmol·L^{-1} LiCl/DMAc eluent was maintained as 0.3 mL·min^{-1}, and the column temperature was set at 313 K. Subsequently, 100 μL each of the prepared cellulose solutions was injected to the HPLC. The standard for the GPC analysis was prepared by dissolving 1-4 g·L^{-1} of polymethylmethacrylate (PMMA, Shodex, molecular mass in the range 1.8×10^{3}–2.0×10^{5} g·mol^{-1}) in a solution of 0.2 wt.% LiCl/DMAc.

Cellulose was dissolved in each RTIL using a hybrid mixer (KEYENCE, HM-500) to achieve initial concentrations in the range 1–30 wt.% and to obtain various viscous and paste-like solutions. The RTILs used in this study, namely, BMI-bis(trifluoromethylsulfonyl)amide (TFSA), BMI-thiocyanate, BMI-chloride, diallylimidazolium (DAI)-chloride, *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium (DEMA)-chloride, and 1-ethyl-3-methylimidazolium (EMI)-bromide, were purchased from Kanto Chemical Co., Inc., Japan. EMI-acetate, at 90 % concentration, was also purchased from Aldrich Chemical Co., Inc. The other RTILs used in this study, namely, BMI-acetate, DAI-formate, DAI-acetate, DEMA-formate, and DEMA-acetate were synthesized by the methodology reported in the literature (Fukaya et al., 2008). In the typical process, RTILs having halides, namely, BMI-chloride, DAI-chloride, and DEMA-bromide, were used as precursors, which were converted into their respective hydroxides using a column filled with an anion-exchange resin (Aldrich, Amberlite IRA 400-OH). The obtained aqueous solutions of RTILs with a pH of 12 were neutralized with either formic acid (Wako, 97 %) or acetic acid (Wako, 1 $\mathrm{mol \cdot L^{-1}}$ aqueous solution) to prepare RTILs functionalized with formate or acetate, respectively. These RTILs were then washed with hexane (Wako, 96 %) and pure water (TOC: 4 ppb, electrical resistance: 18.2 $\mathrm{M\Omega \cdot cm^{-1}}$) supplied from a Millipore Milli-Q system, and vacuum dried overnight at 353 K. All the sample solutions were prepared in a glove bag (Glass-Col) or glove box (Sanplatec) under dry or wet air saturated conditions. The water content in the RTIL solutions was controlled by changing the humidity of the surrounding air. This humidity was controlled by using a 0.1–2 $\mathrm{mol \cdot L^{-1}}$ aqueous solution of calcium chloride (Wako, 99 %) in both the bag and box (Stokes, 1949). The water content in the cellulose solutions was measured with a thermo-balance (Shimadzu AUW120D) and a Karl Fischer titration system (Kyoto Electronics Manufacturing Co., Ltd., MKC-501).

2.2 ^{60}Co γ-ray irradiation

The cellulose solutions were irradiated using a ^{60}Co γ-ray source facility at the Japan Atomic Energy Agency, Takasaki, in the dose range of 5–100 kGy (Gy = J·kg^{-1}) with the dose rates ranging from 5–10 kGy·h^{-1}. The temperature of the sample solutions was controlled using a thermostatic chamber (DTU-1C, TAITEC) during the irradiation. Dosimetric experiments were carried out with an ethanol (Wako, > 99.7 %, HPLC grade)–chlorobenzene (Aldrich, 99.9 %, HPLC grade) dosimeter and an alanine-based dosimeter (Hitachi Cable, Ltd., AMINOGRAY, alanine 70 %, polystyrene 30 %, volume: ϕ3 × 30 mm) in a plastic container (ϕ12 × 50 mm, 4 mm in thickness) (Kojima et al., 1993).

2.3 Measurements

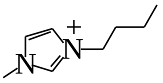
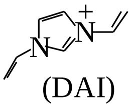
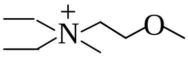
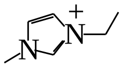
The irradiated sample solutions were subsequently washed with a solution of 5 wt.% LiCl/DMAc to remove any residues of unreacted cellulose, RTILs, and degradation products. The residual matter was rinsed with water on a stainless steel mesh (SUS316, 200 mesh) and then dried overnight at 353 K. The dried sample was weighed in a thermo–balance. Rheological measurement of the sample solutions after γ-ray irradiation was performed on a dynamic viscoelasticity measurement system (TA instruments, ARES RDA-3) at 353 K, in the frequency range of 0.5–100 rad·s^{-1}. Besides, the residual solutions containing unreacted cellulose, RTILs, and degradation products were analyzed in the HPLC system with the GPC column and the refractive index detector. Electrical conductivity of the samples was evaluated using a chemical impedance analyzer (HIOKI, 3522-50) at the frequency of 100 kHz and temperature of 298 K.

3. Results and Discussion

3.1 Radiation modification of cellulose in RTILs

The weight-average molecular weight of cellulose before irradiation was 1.3 × 10^5 g·mol^{-1}, as determined using the Mark–Kuhn–Howink–Sakurada equation and GPC analysis. The paste-like solutions of cellulose were prepared in each RTIL with initial cellulose concentration in the range 10–30 wt.% at 298 K. As listed in Table 1, the concentration of cellulose dissolved in carboxylate–based RTILs was found to be higher than those dissolved in other RTILs.

Table 1 Solubility and gel fraction of cellulose mixed in room temperature ionic liquids under dehydrated condition at 298 K.

Cation	Anion	Concentration of cellulose in paste-like solution (wt.%)
 (BMI)	bis(trifluoromethylsulfonyl)amide	Insoluble
	thiocyanate	Insoluble
	chloride	10
	formate	20
 (DAI)	formate	20
	acetate	20
 (DEMA)	chloride	10
	formate	20
	acetate	20
 (EMI)	acetate	20–30

The paste-like solution obtained by mixing 20 wt.% cellulose in EMI-acetate under dehydrated conditions was first irradiated with γ-rays at a dose of 10 kGy and then washed with a solution of 5 wt.% LiCl/DMAc to remove any residues of unreacted cellulose, degradation products, and EMI-acetate. However, the gel products were not retained in the process. It has been reported that the radiation-induced reduction of chlorophenols in RTILs can occur effectively under dehydrated conditions at a dose of 20 kGy (Kimura et al., 2008, 2010). In the present case, the amount of radiation-induced species was not considered sufficient to cause the cross-linking reaction of cellulose. Therefore, water, which is a source of reactive species such as hydroxyl radicals and hydrated electrons produced by ionizing radiation, was added to the dried cellulose solution to enhance the radiation-induced cross-linking of cellulose. The cellulose EMI-acetate solution with a water content of 18 wt.%, was prepared under humidity-controlled air conditions and left overnight to form a physical gel. The gel thus obtained could be completely dissolved in a 5 wt.% LiCl/DMAc solution. The physical gel was irradiated with γ-rays at a dose of 10 kGy, followed by washing with a 5 wt.% LiCl/DMAc solution to obtain an insoluble residue.

The physical properties of the insoluble product thus obtained were evaluated by dynamic viscoelasticity measurements (Techwipharat et al. 2008; Zhou et al. 2008). The interactions among the cellulose chains of the physical gel are weak and reversible, and the gel reverts to a sol at temperatures above 353 K. Figure 1 shows the storage modulus (G′) and loss modulus (G″) of the solution containing 20 wt.% of cellulose in EMI-acetate before and after irradiation measured at 353 K. The G′ and G″ values of the as-prepared physical gel (before irradiation) increase with frequency, without showing the crossover point of G′ and G″. This indicates that the as-prepared sample (before irradiation) is a sol at 353 K (Song et al., 2011). On the other hand, after irradiation, the G′ curve of the insoluble product obtained by irradiation at a dose of 20 kGy was almost constant, while that of the G″ increased with frequency. This implies that the irradiated sample is a gel at 353 K. Based on these results, the obtained insoluble product can be considered as a cellulose gel.

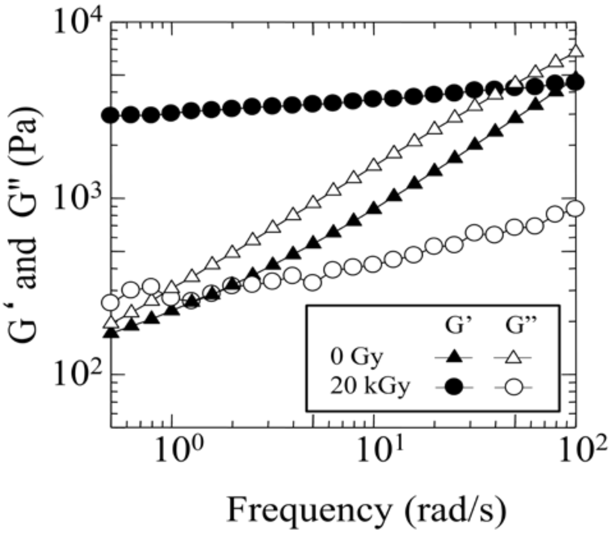


Figure 1 Dynamic viscoelasticity measurement of 20 wt.% cellulose in EMI-acetate, containing 18 wt.% of water at 353 K under aerated conditions, before and after γ-ray irradiation at 20 kGy.

The cellulose gel fraction was separated from the γ-ray irradiated solution of 20 wt.% cellulose dissolved in EMI-acetate with 18 wt.% of water at 298 K under aerated conditions. The soluble part, i.e., the sol, was evaluated using the GPC system with the refractive index detector. The peak retention time of 40.0 min could be assigned to the cellulose before irradiation. However, with increase in irradiation dose, the retention times slowly shift towards higher values, as shown in Figure 2.

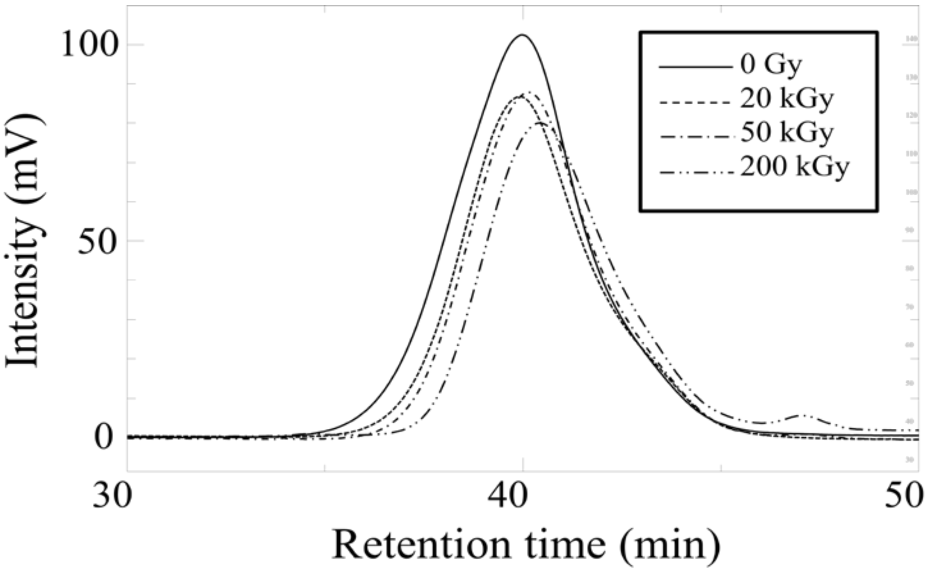


Figure 2 Gel permeation chromatograph of the solution of 20 wt.% cellulose dissolved in EMI-acetate with 18 wt.% of water at 298 K under aerated conditions, compared with a neat cellulose gel at doses of 0 Gy (line), 20 kGy (dot line), 50 kGy (chain line), and 200 kGy (two-dot chain line).

For the absorbed dose of up to 20 kGy, the intensity of the peak at 40.0 min was clearly reduced by approximately 13 %. This could be attributed to the fact that the irradiation products mainly consist of the cellulose gel and degradation products. The weight-average molecular weight of the cellulose samples at the dose of 0, 20, 50, and 200 kGy was found to be 1.3×10^5, 1.1×10^5, 1.0×10^5, and 8.8×10^4 $g{\cdot}mol^{-1}$, respectively, as evaluated using the PMMA standard solution. As mentioned earlier, it has been reported that the degree of polymerization and the weight-average molecular weight of cellulose dissolved in BMI-chloride are reduced by approximately 50 % at the dose of 200 kGy (Hao et al. 2012). In the present study, the rate of decrease in the weight-average molecular weight of cellulose dissolved in EMI-acetate was found to be 32 % at the same dose of 200 kGy. This is lower than that reported for cellulose dissolved in BMI-chloride. The intensity of the peak at the retention time of 47.0 min increased when the dose was greater than 20 kGy (Figure 2). This peak can be assigned to the irradiation products corresponding to the weight-average molecular weight of 7.1×10^3 g·mol^{-1}.

3.2 Mechanism underlying the formation of cellulose gels in RTILs

In general, the solid cellulose is decomposed by ionizing radiation (Charlesby et al. 1957; McLaren 1978; Kumakura et al. 1979; Charlesby 1995; Takacs et al. 1999; Driscoll et al. 2009). Upon γ-ray irradiation, radicals emerge preferentially as a result of the fracture of C-H bonds in the weakened 1 and 4 positions of cellulose. Subsequently, the direct cleavage of the chemical bonds occurs at these positions in the polymer chains to produce cellulose of lower molecular weight (Yershov et al. 1977; Hao et al. 2012). However, in this study, cellulose gel was produced when the solution of 20 wt.% cellulose dissolved in EMI-acetate was irradiated under humid conditions without cross-linking agents.

Reactive intermediates, such as solvated electrons, hydrogen atoms, positive ions, excited molecules, and radicals, are formed in the organic solvent (Woods et al., 1994.).

$$S \rightsquigarrow e^{-}_{solv},\quad H,\quad S^{+},\quad S^{*},\quad S^{\bullet} \qquad (2)$$

where S, e^{-}_{solv}, and H are represent solvent, solvated electrons, and hydrogen atoms, respectively. The rate constants corresponding to the reaction of radiation-induced reductive species, such as solvated electrons, with some aromatic and halogenated organic solutes is typically higher than the corresponding diffusion-controlled rate constants in RTILs under dehydrated conditions (Wishart et al., 2003; Wishart et al., 2005; Kimura et al., 2008; Kimura et al., 2010). The cellulose gel, however, was not produced in EMI-acetate under dehydrated conditions. The solvated electrons have low reactivity toward cellulose as a saturated hydrocarbon, and are not related to the radiation-induced cross-linking of cellulose under the conditions.

The cellulose EMI-acetate solution having 18 wt.% of water was irradiated with γ-rays to produce the cellulose gel as stated above. In this reaction, water is decomposed by the ionizing radiation, resulting in the formation of a hydroxyl radical, hydrated electron, hydrogen atom, proton and hydroxide ion (Getoff et al., 1996).

$$H_2O \rightsquigarrow \cdot OH,\quad e^{-}_{aq},\quad H,\quad H^{+},\quad OH^{-} \qquad (3)$$

The hydroxyl radicals, in particular, contribute to the production of cellulose gel, owing to their high reactivity toward saturated hydrocarbons and high yield upon water radiolysis (Buxton et al., 1988). Besides, the hydroxyl radicals, hydrated electrons (e^{-}_{aq}) and the electrons solvated by the EMI-acetate (e^{-}_{solv}) also react with the alkylimidazolium of the EMI-acetate to form alkylimidazolium radicals (Behar et al., 2001; Wishart et al., 2005).

$$\cdot OH + EMI^{+} \rightarrow HO\text{-}EMI^{+\cdot} \quad (4)$$

$$e^{-}_{aq} / e^{-}_{solv} + EMI^{+} \rightarrow EMI\cdot \quad (5)$$

As mentioned earlier, γ-ray irradiation of the solution of 20 wt.% cellulose dissolved in EMI-acetate under dehydrated condition did not result in the formation of gel. Therefore, the solvated electrons and alkylimidazolium radicals cannot be related to the radiation-induced cross-linking of cellulose. On the other hand, hydroxyl radicals are considered to oxidize the carbon atoms of cellulose to produce cellulose radicals (Isogai et al., 1998).

$$[Cellulose]\text{-}H + \cdot OH \rightarrow [Cellulose]\cdot + H_2O \quad (6)$$

There is a possibility that the cellulose radicals are formed in the solid phase or in another organic solvent upon γ-ray irradiation. However, the macro-sized cellulose radicals would not diffuse easily in the solid phase. Besides, the solubility of cellulose is less than 10 wt.% in organic solvents, such as chloroform in dimethylsulfoxide, *N*-methylmorpholine-*N*-oxide, LiCl in DMAc, and calcium chloride in methanol. In contrast, the radiation-induced cellulose radicals in EMI-acetate readily diffuse more easily than that in the solid phase to facilitate cross-linking reaction, and solubility of cellulose in EMI-acetate is higher than that in the organic solvent systems listed. Based on these observations, following reaction paths are proposed for the formation of the cellulose gel.

$$[\text{Cellulose}]\cdot \quad + \quad [\text{Cellulose}]\cdot \quad \rightarrow \quad [\text{Cellulose}]\text{-}[\text{Cellulose}] \qquad (7)$$

The cellulose having radicals at the 6th carbon atom is expected to participate in the cross-linking reaction because the side chain of the polysaccharide derivatives is considered to be the cross-linking position (Saiki et al., 2010; Saiki et al., 2011).

3.3 Gel fraction of cellulose in RTILs under several conditions

It has been reported that structure of the cellulose polymer chains in EMI-acetate tends to change as a function of the concentration of cellulose and the temperature of γ-ray irradiation (Song et al., 2011). This effect was further analyzed in this study, as the yield of the obtained cellulose gel was found to depend on the oriented structures of the cellulose polymer chains. The yield of the gel obtained by γ-ray irradiation of cellulose dissolved in EMI-acetate was estimated in terms of the gel fraction by the following equation:

$$\text{Gel fraction (\%)} = (W/W_0) \times 100 \quad (8)$$

where W_0 and W are the initial mass of the dried sample before irradiation and the final mass of the insoluble product obtained after irradiation, washing, and drying, respectively. The gel fraction of the cellulose gel in EMI-acetate having 18 wt.% of water under air-saturated conditions increased with increase of dose at 298 K, and reached a maximum value of 17 % at the dose of 10 kGy, as shown in Figure 3.

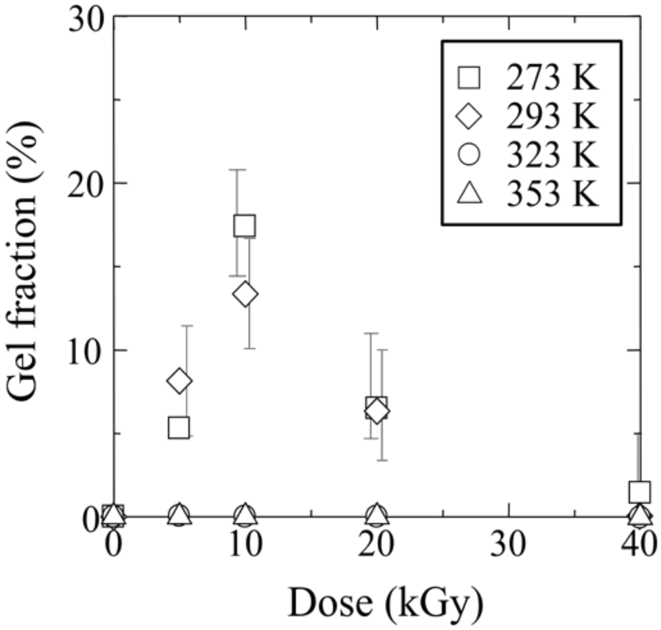


Figure 3 Gel fraction of 20 wt.% cellulose in EMI-acetate containing 18 wt.% of water under aerated conditions plotted as a function of the absorbed dose.

The gel fraction does not exist at temperatures above 323 K. The physical gel begins to revert to a sol above 323 K (Song et al., 2011), and becomes a solution at 353 K under dehydrated condition. For the solution with lower viscosity, the scission reaction is dominant by ionizing radiation (Nagasawa et al. 2000). Therefore, the optimal production of the cellulose gel was obtained under the physical gel condition at temperatures less than 298 K. In addition, a paste-like solution of 20 wt.% cellulose in DEMA-formate with 18 wt.% of water under air-saturated conditions at 298 K was also irradiated at a γ-ray dose of 10 kGy. This resulted in the formation of cellulose gel with a yield of 19 %. However, the formation of cellulose gel was not obtained in other RTILs in the presence of water, as listed in Table 1. This could be attributed to the fact that the cellulose was heterogeneously dispersed in these RTILs, as opposed to that in the EMI-acetate and DEMA-formate.

Furthermore, the cellulose at an initial concentration of 1–50 wt.%in EMI-acetate having 18 wt.% of water under air-saturated conditions at 298 K was also irradiated at a dose of 10 kGy. For initial concentration higher than 40 wt.%, the cellulose was found to disperse heterogeneously in EMI-acetate. The gel fraction of the obtained cellulose gel is illustrated in Figure 4. The formation of cellulose gel is effective in the initial concentration range of 20–30 wt.%. On the other hand, the cellulose solutions had low gel fractions for their initial concentrations either lower than 10 wt.% or higher than 40 wt.%.

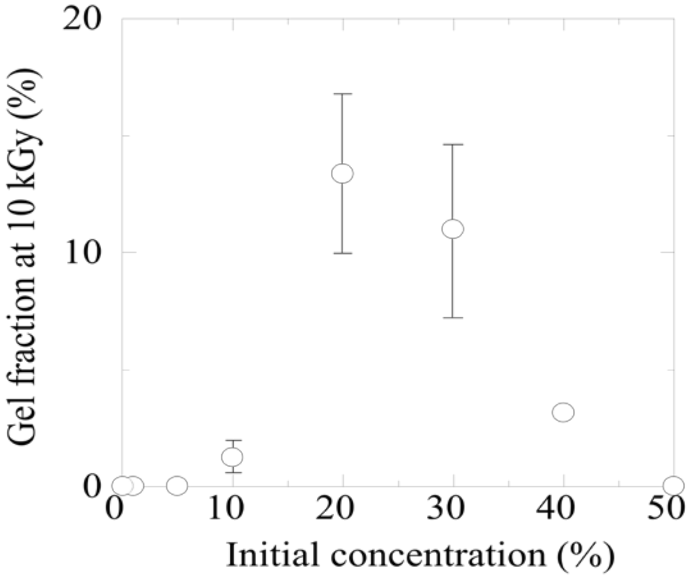


Figure 4 Initial concentration dependence of the gel fraction of cellulose in EMI-acetate having 18 wt.% of water at 298 K under aerated conditions at 10 kGy.

In general, when polymers are irradiated with ionizing radiation, both the cross-linking and scission reactions occur simultaneously. The scission reaction is dominant over the cross-linking reaction when the concentration of polysaccharides in the organic solvent is less than approximately 10 wt.% (Tabata et al., 1991; Nagasawa et al., 2004). However, irradiation of the samples in the paste-like state is effective to facilitate the cross-linking of other polysaccharide derivatives (Fei et al., 2000; Zhao et al., 2003; Nagasawa et al., 2004). Besides, a paste-like solution of cellulose dissolved in EMI-acetate can be prepared for the concentration range of 20–30 wt.%. In the present study, the ratio of degradation to cross-linking density (p_0/q_0) was estimated using the Charlesby–Rosiak equation (Olejniczak et al., 1991):

$$\mathrm{s} + \mathrm{s}^{1/2} = \frac{p_0}{q_0} + \left(2 - \frac{p_0}{q_0}\right)\frac{\mathrm{D_v} - \mathrm{D_g}}{\mathrm{D_v} - \mathrm{D}} \tag{9}$$

Here, s, D, D_g, and D_v are the sol fraction, absorbed dose, gelation dose, and virtual dose, respectively. For the solution of 20 wt.% of cellulose in EMI-acetate at 298 K with 18 wt.% of water under air-saturated conditions, the value of p_0/q_0 was estimated to be 1.86. The value implies that the scission reaction occurs more effectively than the cross-linking reaction, resulting in a low cellulose gel yield of 17 %. The p_0/q_0 values for 10, 30, and 40 wt.% of cellulose in EMI-acetate at 298 K having 18 wt.% of water under air-saturated conditions were estimated to be 1.97, 1.74, and 1.92, respectively.

The respective effects of the water content on the gel fraction of cellulose in EMI-acetate were also investigated by γ-ray irradiation. The gel fraction of cellulose increases with water content, as shown in Figure 5. As mentioned earlier, the radiation-induced cross-linking of cellulose is considered to be initiated by the hydroxyl radicals. The sample solution containing 34 wt.% of water, which was partially clouded, was irradiated with γ-rays. However, cellulose gel was not obtained under this condition. The crystallization of the cellulose became more pronounced with decrease in the concentration of the RTILs in the solution. The cellulose solution containing 34 wt.% of water is considered to be the similar to that of the solid cellulose. Hence, the scission reaction of cellulose would have been dominant.

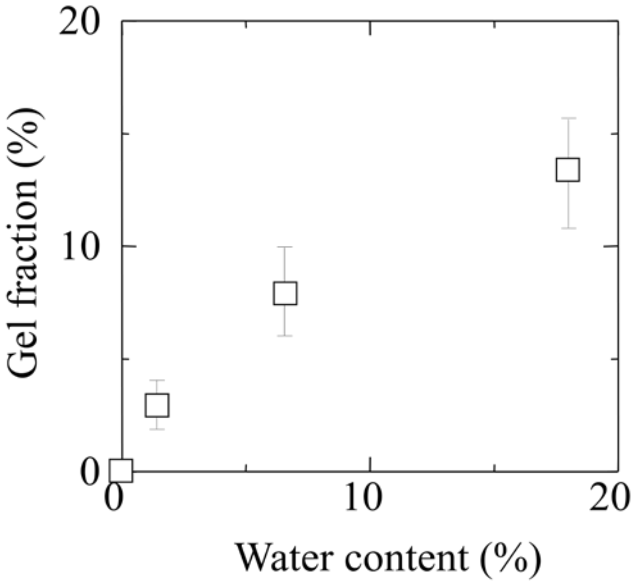


Figure 5 Water content dependence of the gel fraction obtained by γ-ray irradiation of 20 wt.% cellulose in EMI-acetate at 298 K under aerated conditions at 10 kGy.

3.4 Electronic conductivity of cellulose gel

Recently, polymer ion gels that are swollen with RTILs have been applied as electrolytes in dye-sensitized solar cells (Ueno et al., 2008), electroactive polymer actuators (Imaizumi et al. 2012), and thin-film transistors (Lee et al., 2007), owing to thier excellent chemical and thermal stabilities, wide potential windows, and high electrical conductivities of 10^{-2}–10 mS·cm^{-1}, which depend on the type of RTIL used in the process (Kitazume et al., 2005; Lodge, 2008). In this study, cellulose gels were swollen with water, methanol, ethanol, dichloromethane, DMAc, EMI-acetate, and DEMA-formate. The swelling ratio of cellulose gel in EMI-acetate was 3.7 g swollen gel/g dried gel. The electronic conductivity of the cellulose gel containing

EMI-acetate, as estimated by the chemical impedance method at 298 K was found to be 3.0 mS·cm^{-1}. This is sufficiently higher than the required electronic conductivity of 0.1 mS·cm^{-1} for the organic solid electrolytes (Ohno, 2006). The conductivity of EMI-acetate was the same with that of the cellulose gel containing them. Therefore, cellulose gel has great potential for applications in optoelectronic and medical devices as a fascinating biopolymer and sustainable raw material.

4. Conclusion

For the first time in this study, we have demonstrated the possibility of producing cellulose gels by γ-ray irradiation of cellulose in RTILs under humid conditions. Water was found to be essential for the formation of the cellulose gel, as the hydroxyl radicals formed by the radiolysis of water play an active role in the cross-linking of cellulose. RTILs having hydrophobic imidazolium/ammonium and proton-accepting carboxylate groups were found to be suitable mediums for the production of cellulose gels. The gel fraction could be controlled by adept regulation of following conditions: initial concentration of cellulose, irradiation temperature, water content, and the absorbed dose. The cellulose gel thus obtained had an electronic conductivity of 3.0 mS·cm^{-1}, showing great potential for applications in optoelectronic and medical devices.

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