Application of Ionic Liquids on Microscopic Observation of Hydrated Materials

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Electron microscopic techniques that are used as a standard method characterize micro- and nano-structured materials have been extended for observing wet materials. Most of the microstructures of solid materials, such as ceramics, metals, polymers and composites in their dry conditions, are characterized by electron microscopy. However, the observation methods for hydrous materials have still been under development because the wet condition is not suitable for the electron microscopy under high vacuum conditions. This difficulty in the characterization of the hydrous materials is a barrier to the research progress related to wet materials processing.

In this review paper, developed observation methods with the aid of a hydrophilic ionic liquid (IL) for various kinds of hydrated materials are reported. By the developed observation methods, the characterization of hydrous materials, such as seaweed, agar gel and a HAp green body, is enabled and extended to a range of related fields. Based on the interaction between water molecules and hydrophilic IL, the mechanism for the observation of wet materials using the hydrophilic IL has been clarified and the molecular dynamics of the IL and solvents have been studied. In addition, an IL-inorganic composite material was successfully fabricated by mixing of IL and montmorillonite clay in the proper ratio, which suggests possibility to invent novel electron conductive transparent thin films.

1. Introduction

Electron microscopes are presently employed as indispensable material characterization tools due to the advancement in technologies especially in high resolution performance images, high resolution analysis equipments and 3D observation abilities [1-5]. Among various electron microscopy techniques, the scanning electron microscopy (SEM) has been popularly used in the scientific community over 40 years due to its wide applications in metals, semiconductors, ceramics, medical and biological field. Compared to solid materials, the sample preparation for biological or other wet materials to be observed by SEM is complicated and even difficult to maintain the morphology in a vacuum condition. Therefore, to observe the exact morphologies of these wet samples, new methodologies are being searched.

Ionic liquids (ILs) are organic fused salts that consist of ions and retained fluid at room temperature (RT). Some ILs exist below 100℃ [6]. These compounds consist of an organic cation and an organic or inorganic anion. The cation, which has a large and asymmetric structure, prevents the formation of a crystal structure, such as NaCl, and hence it remains as a liquid at RT. Most of the ILs are classified in seven families based on the structures of their cation and anion parts (Figure 1). The different combinations of cations and anions significantly affect the IL properties, such as polarity, melting point, hydrophilicity, hydrophobicity, etc. ILs have unique physical properties, such as negligible-vapor pressure (up to 5×10^{-9} Torr), non-flammability, chemical/ thermal stability, high ionic conductivity (up to 120 mS cm_{-1}) and wide electrochemical windows (up to 5.8 V). ILs are used as solvents in various chemical reactions [7-11], or in dispersion of carbohydrate polymers such as cellulose and starch etc [12-14]. Furthermore, a composite gel mixed with IL is used in drug delivery systems and fabrication of contact lenses [15-17]. Besides these applications, ILs mixed with samples can be directly observed in the electron microscope due to their negligible vapor pressure and high conductivity [18-21]. Although some reports suggest that wet materials (seaweed, chicken tissue etc) mixed with hydrophilic IL can be observed by SEM without any additional conducting coating [22, 23], still this technique needs to be further applied to other kind of wet materials.

In this review paper, an optimization method for the microscopic observations of hydrous materials is presented, and the study of the observation mechanism

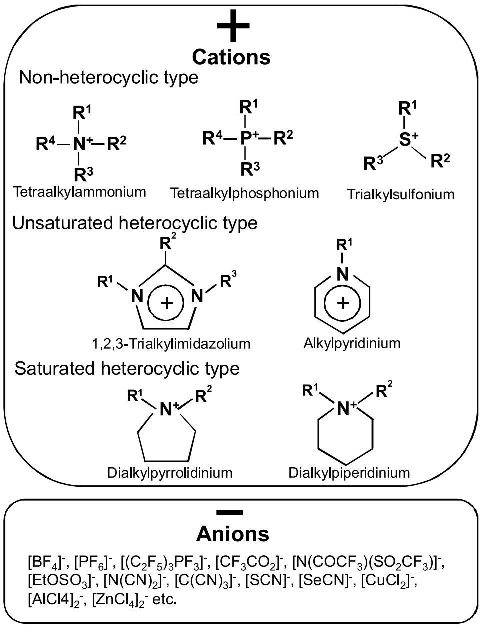

Figure. 1. Types of cations and anions that constitute the ILs.

using a hydrophilic IL is proposed. Furthermore, the fabrication of composite materials with the aid of various ILs has been described with the aim of enhancing the conductivity of materials in various fields.

2. Observation method of hydrous materials with the aid of IL by an electron microscope

The unique properties of RTILs, such as conductivity and negligible vapor pressure, have opened up new scientific methodologies under vacuum conditions. In 2005, Scherson et al. reported that RTILs can be used under a high vacuum condition (less than 5×10^{-9} Torr) [24]. Subsequently, RTILs were the focus as solvents for vacuum technology. This discovery is a breakthrough method in this scientific field, which defies the common wisdom that liquid evaporates under vacuum conditions. Interestingly, samples containing ILs can be observed using an electron microscope (SEM / TEM) under high vacuum conditions. Generally, the samples for electron microscopy need a coating of osmium, platinum or carbon. However, ILs provide a conductive and a negligible vapor pressure properties to the samples though they are liquids. It is reported that electrons, which are injected into the ILs, are stable and move into the liquid phase of the ILs under a high accelerating voltage condition [25]. Based on this discovery, Kuwabata et al. developed the observation method of insulating samples using ILs [18,19,21,22,26]. The insulating star-like sand was observed using a hydrophobic IL, [EMI][TFSI], and abrasive paper was also observed using a hydrophobic IL, [BMI][TFSI]. The TiO_2 nano-tube layers in a wet condition using droplets of ILs were characterized in order to study the wetting behavior [20]. Surprisingly, the possibility of microscopic observations of materials containing water was also suggested, and many researchers reported the fine morphology and observation method of various insulating samples using ILs. The cellular ultrastructure of a cultured human cell was characterized using hydrophilic and hydrophobic ILs [27-29]. It has been revealed that hydrophilic ILs are useful for observing the morphology of wet materials compared to hydrophobic ILs. By using hydrophilic ILs, the fine structure of a chromosome was observed [30]. Various treatments on ILs have been examined, such as pre-warming, well-mixing, reduced concentration, mixing with platinum blue staining, etc., to optimize conditions. It is considered that the ultrastructure of the basidiospore ornamentation is important in the delimitation of taxa for fungi. The use of hydrophilic ILs has enabled the determination of the ultrastructure of the basidiospore ornamentation [31]. Moreover, using Choline-like ILs, which have high penetration ability, the morphology of seaweed and food samples was observed [23].

However, in this process, one must take note of the hygroscopic properties of the hydrophilic IL wherein the absorption of some amount of water from the atmosphere occurs. Depending on the amount of absorbed water, the IL properties, such as viscosity, conductivity and polarity, can be drastically changed. Therefore, we need to optimize the observation method based on the interaction between water molecules within hydrous sample and hydrophilic ILs. In order to cover the entire range of the inorganic and hydrous materials research fields, biological polymers (agar gel), ceramics green bodies (hydroxyapatite) and biological materials (seaweed) will be selected. Biological polymers, ceramics green bodies and biological materials were selected as the polymer materials, insulated inorganic materials and organic materials, respectively.

2.1. Biological polymer (Agar gel)

Among various materials, agar gel in its wet condition is popularly used in biology, medicine and food industries. Especially in biochemistry, the agar gel is widely used in culturing media of microbes and in cataphoresis. Furthermore, the agar gel is also used as a gelling agent for various ceramic forming processes due to hazardousness and non-toxicity as compared to acryl amides in traditional gel-casting method. In this method, the agar gel enables to make complex network along with well distributed ceramic particles [32-34]. However, morphology of such complex network structure in wet conditions is difficult to be observed accurately under an electron microscope in vacuum. Therefore, we need to develop the simple observation method for hydrous agar gel.

With this concept, the observation method for agar gel with the aid of hydrophilic IL; 1-butyl-3-methylimidazolium tetrafluoroborate; [BMIM][BF_4] was developed. It has been noticed that addition of a small amount of water to hydrophilic ILs changed their properties due to the interaction with the water molecules [35-37]. Thereby, we optimized the IL treatment on the basis of the interaction between water molecules and hydrophilic IL [38-40]. Figure 2 shows the FE-SEM images of agar gel in IL with 15-95 mol % water concentration. From the FE-SEM and size retention before and after IL treatment results, it was found that the exact morphology of agar gel in various swelling condition can be achieved by adjusting the water concentrations in the range of 15-30 mol % in the samples. An exact morphology of swelled agar gel was clearly observed with less than 1 % difference even in a paste condition with large amounts of liquid phase. The surface morphology was not changed even if the sample was kept under vacuum at 60 °C for 24 h and in FE-SEM chamber. This electron microscope observation will be very important for understanding the exact morphology of water-containing materials. In addition, the approach on microscopic observation of wet agar gel in different swelling condition opened up a new methodology to observe hydrated samples in FE-SEM.

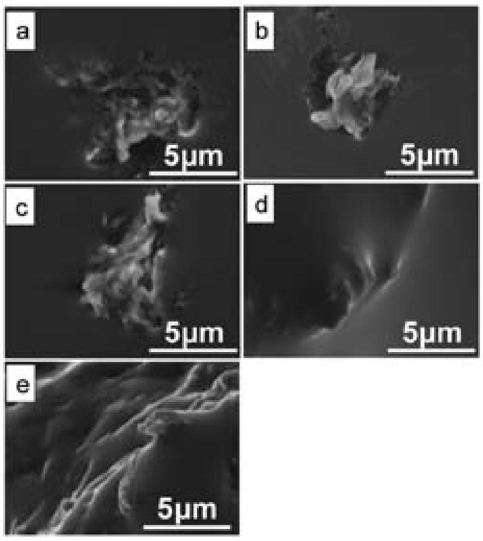

Figure. 2. FE-SEM images of agar gel in IL with (a) 15, (b) 30, (c) 60, (d) 80 and (e) 95 mol% water concentration. The accelerating voltage for FE-SEM observation was 5.0 kV.

2.2. Ceramics green body (Hydroxyapatite)

Among the various types of calcium phosphate ceramics, hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAp] is a well-known biocompatible material and is naturally found as one of the major components of bone and tooth [41,42]. As-synthesised HAp ceramics show both osteoconductivity and osteoinductivity and directly bonds to the living bone through the native apatite phase [43,44]. However, for enhanced bone integration and mechanical interlocking between implanted devices and the newly grown bone tissues, particular attention must be paid to the processing of the porous HAp body [45]. To establish enhanced processing conditions for ceramics, it is necessary to understand the complex structure of the green body. Thus, it is essential to develop new techniques for microscopic observations of ceramic bodies in the hydrated form.

Therefore, our research group attempted to develop a simple and convenient method for observing the microstructure of the hydrated porous HAp green body using a hydrophilic IL. The FE-SEM observations (Figure 3) showed that the as-prepared porous green body had a pore diameter of approximately 300-600 μm, which gradually decreased to approximately 200-400 μm during drying in a humid chamber from 90 to 50 % relative humidity. When HAp sample is added into IL, it bonds with water molecules within the HAp-polymer

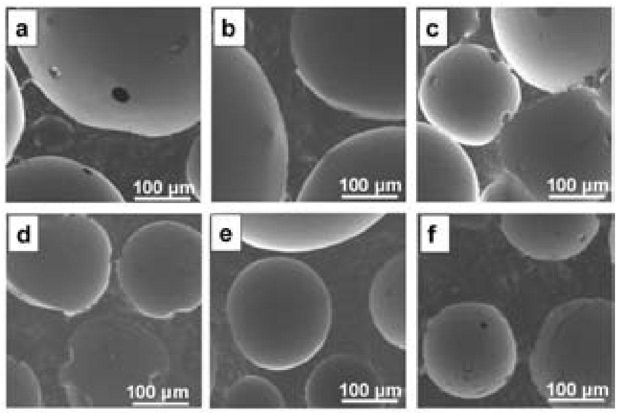

Figure. 3. FE-SEM images of (a) the as-prepared porous HAp green body just after removal from the mould and of the specimens treated in the humid chamber at (b) 90, (c) 80, (d) 70, (e) 60 and (f) 50% relative humidity.

network structure, thereby forming a weak hydrogen bond entangling with the HAp particles surrounding the porous body. This bonding resulted in the formation of an IL-water-HAp-polymer complex, in which the IL acts as a conducting media; additionally, the formation of weak hydrogen bonds between the IL and the water further prevents the porous HAp body from dehydration caused by evacuation of FE-SEM chamber. Further, the limitations of observing the hydrated porous HAp green body by micro-focused X-ray CT were revealed [46,47]. Thus, we successfully revealed the solidification behavior of a water-HAp-polymer complex structure during the gelcasting process. This simple method of observation can also be applied to studies on microstructures of a wide range of nonconductive ceramic materials during wet processing.

2.3. Biological materials (Seaweed)

It has been reported that the microstructures of biological materials mixed with ILs can directly be observed by electron microscopy [18,21,22]. However, some reports suggested that wet materials, such as seaweed, chicken tissue, and etc, mixed with a commercially available IL are not suitable for observation by SEM [23]. Furthermore, an excess IL around the sample is reported to be a problem for SEM observation. Therefore, a modification in the sample preparation method is required.

We have proposed that the exact morphology of the wet material such as agar gel or gelcast ceramics can be observed by FE-SEM. However, microstructures of biological materials such as seaweed could not satisfactorily be observed by applying a similar methodology. Therefore, we have developed a modified method to observe the exact morphology of seaweed using hydrophilic IL; 1-butyl-3-methylimidazolium tetrafluoroborate; [BMIM][BF_4].

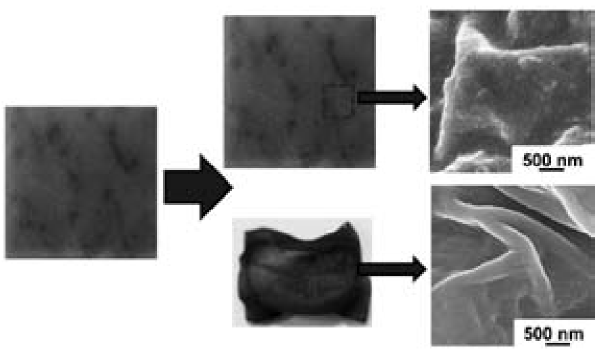

Figure. 4. Optical microscope and FE-SEM images of the seaweed before and after IL treatment.

We suggested that the optimization method of seaweed as biological materials for FE-SEM observation was required. This is because the observation mechanism for biological materials was different from gel materials. It is then concluded that the osmotic pressure of biomaterials in IL solution affects its configuration. Moreover, an excess IL around sample disturbs acquisition of a fine morphological image; however, a centrifuge with optimized rotation speed enables to solve the problem [48]. Our developed methodologies, for biological materials using the typical commercially available IL, are novel techniques that allow observing the exact morphology without any alteration.

3. Observation mechanism

We were able to establish the microscopic observation methodology of hydrated materials (Section 2). It can be concluded that the water concentration within the hydrous sample after the hydrophilic IL treatment is beneficial for the optimization during the observation method. The interaction between the water molecules in the hydrous sample and hydrophilic IL has occurred during the sample preparation. Therefore, we focused on the molecular dynamics and studied the observation mechanism of hydrous materials using hydrophilic IL and agar gel as a sample.

Some researchers have started to point out the lack of understanding of the IL structure that affects its physical properties when using the ILs. Therefore, the possible presence of water in the RTILs affects their solvent properties, such as electron conductivity, viscosity, polarity, and etc., has been reported using a variety of experimental techniques and theoretical calculations [49-53]. These results showed that both cations and anions of IL played a significant role for the formation of hydrogen bond with a water molecule, although anions always participate dominantly [54, 55]. Also, the interaction between OH (derived from water) and IL (both anion and cation) in different circumstances are observed by FT-IR spectroscopy and Raman spectroscopy [56-59].

With this concept, the observation mechanism was studied in terms of hydrogen bond between anionic part of IL and water molecules (also water molecules within agar gel) by Raman spectroscopy and differential scanning calorimeter (DSC). Based on the result of the in-situ Raman spectroscopy, DSC and FE-SEM, it is

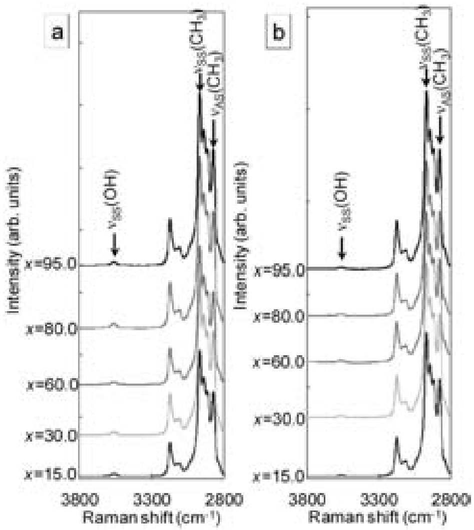

Figure. 5. The Raman spectra of IL solution after sample preparation treated with different water concentrations (x: unit of water in mol %). (a) Keeping in a desiccator for 3 h, (b) keeping in a desiccator for 3 h + under vacuum condition at 60 °C for 24 h. The arrows show the peak of the $\nu_{SS}(OH)$, $\nu_{SS}(CH_3)$ and $\nu_{AS}(CH_3)$ stretching vibration region.

concluded that the exact morphology of agar gel can be observed when IL penetrate into agar gel completely. Figure 5a shows the water molecules within the agar gel, which were taken by IL when the samples were kept in a desiccator for 3 h as a preparation condition for FE-SEM observation. IL and water exist as $BF^-_4 \cdots HOH \cdots BF^-_4$ via weak hydrogen bond indicated as $\nu_{SS}(OH)$ even in vacuum condition due to its strong bonding ability (Figure 5b). It is suggested that the water molecules within agar gel were displaced by IL owing to the similar weak hydrogen bond formation. However, when there is not enough IL, water molecules are not completely taken up by IL. Therefore, it could be understand that morphology of agar gel was changed due to easy evaporation of residual water within agar gel. From these results, it was found that the exact morphology of agar gel or any gel materials could be obtained by adjusting water concentrations in the range of 15-30 mol % in the samples [38-40]. Thus, the agar gel or any other materials under wet condition excluding biological materials can be observed without drying using the electron microscopy based on this anomalous mechanism. In addition, the information on the specific interaction between molecules can provide further understanding for the future research on molecular dynamics study.

4. Fabrication of the intercalated compounds using various kinds of ILs

Clay minerals are remarkably often used in our daily life due to their abundant resources, high sorption capacity, ion exchange properties and low cost. Clays have layer structures and are used as host materials for fabricating hybrid composites [60]. Among various applications, thermal stability of clay - organic compound has been provided by improving physical properties and reducing flammability [61,62]. IL modified clays are recently paid attention due to ILs unique properties such as negligible vapor pressure, nonflammability and electrical conductivity for fabricating inorganic clay - organic intercalation compounds with high thermal stability and composite materials with improved flame retardant property [63,64]. However, most of the cases intercalation was carried out using polymer and IL together. In addition, some researchers studied the intercalation of clay by various ILs [65,66]. Thereby, we focused on IL intercalation into clay without any additional compound or solvent torealize a more convenient and eco-friendly method is discovered.

In recent years, transparent electrically conducting thin films such as Indium tin oxide (ITO) and Antimony tin oxide (ATO) are utilized for a solar battery, liquid crystal and organic electroluminescence (EL) display [67,68]. However, other possible materials for transparent electrically conducting thin films are still being researched.

Hence, the direct intercalation of an IL into the montmorillonite (M) is attempted and fabricated the IL-M intercalated compounds using four kinds of ILs (M_{IL}). These ILs consist of the imidazolium or ammonium-type cation with different kinds of anions. Four kinds of IL and montmorillonite intercalated compounds was directly fabricated by mixing IL of different salts (imidazolium and ammonium) and cation size and montmorillonite clay [69]. The XRD results showed that the cation size of the ILs influenced the extent of crystal swelling, and the TEM-EDS further confirmed the intercalation of each IL into montmorillonite interlayer. The crystal swelling behavior as observed by XRD was further verified by TEM-SAED. It can be seen in Figure 6 that the structure consists of the swelled-like area and it maintains the crystal structure. From the cation exchange capacity (CEC) results and mathematical calculations, extent of intercalation and arrangement of cations in the interlayers of montmorrillonite clay is

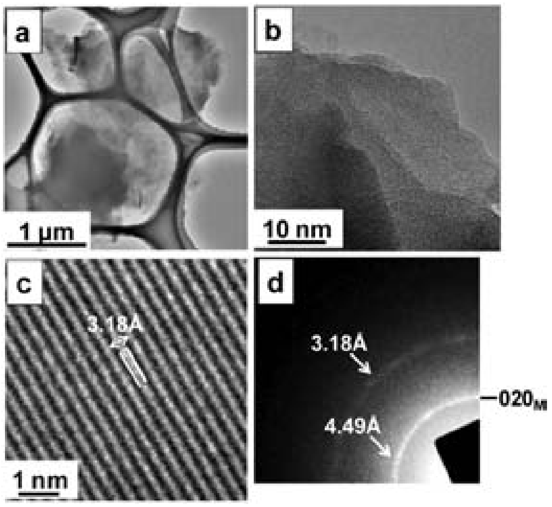

Figure. 6. TEM images of the intercalated compound in bright-field images (a)(b), high-resolution image (c), and SAED pattern in which the Debye rings are measured (d). The subscript M is derived from montmorillonite.

proposed. In addition, the XRD and CEC results confirmed that IL intercalated into the montmorillonite's interlayer within 1 min of mixing and attained a saturation level very rapidly. The TG-DTA measurement of M_{IL} intercalated compounds showed an improved thermal stability as compared to IL.

This observation technique is useful to understand the intercalated behavior and swelling structure of layered materials with the liquid phase. In addition, a low sheet resistivity of montmorillonite-IL composite indicates a possibility of such a better thermally stable material as a transparent electrically conducting thin film.

5. Summary and outlook

In this review paper, it is concluded that the developed methodology using an IL helped to observe the hydrated materials in various fields by the electron microscopy.
The materials can be classified for observation as follows:
A. Hydrated insulating materials, such as an agar gel, a HAp green body and montmorillonite swelled by water, and
B. Biological materials, such as seaweed, which were maintained by osmotic pressure.
Each optimization method was described as the following and shown in Figure 7.

A: (1) Sample was treated with IL and adjusted by 30 mol % water concentrations. (2) Sample was kept in a desiccator for 2 h and then put under vacuum for 24 h. (3) To remove the excess IL from around the sample, the sample was centrifuged.

B: (1) Sample was preserved by each sampling method for adjusting the osmotic pressure as a natural environment. (2) Sample was treated by IL diluted in water to maintain its osmotic pressure and adjusted using a 30 mol % water concentration. (3) Sample was kept in a desiccator for 2 h and then put under vacuum for 24 h. (4) To remove the excess IL from around sample, the sample was centrifuged.

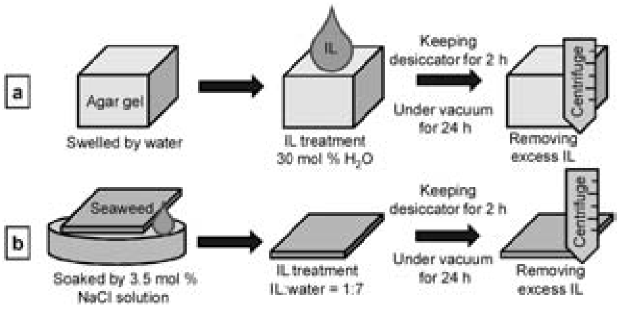

Figure. 7. Observation method for (a) hydrated insulating materials and (b) biomaterials.

These observation techniques are useful for understanding the exact morphology and behavior of any kind of hydrated materials, including biological materials and inorganic materials. The understanding of a visualization mechanism using a hydrophilic IL can also contribute to studying the molecular dynamics of the IL and solvents, such as water and ethanol. In addition, the fabrication of the montmorillonite-IL composite materials willead production of a better thermally stable material as a transparent electrically conducting thin film. Thus, these applications with the aid of ILs in this review will contribute to further development of science and technology. Although ILs are not widely applied except for chemical scientists, it has a great potential for scientific research under vacuum condition. Therefore, this developed observation methodology, molecular dynamics study of IL and solution, and fabrication of composite materials using IL presented in this review might provide better information for readers who start to IL research in vacuum condition. Hopefully, many researchers can develop their works related to IL through the application of our techniques and studies.

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