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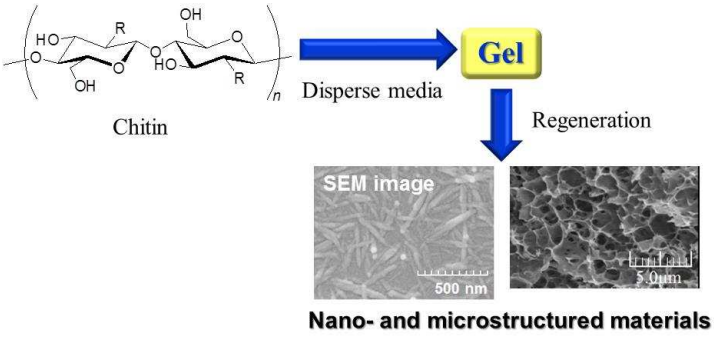

Regeneration from chitin gels with suitable disperse media efficiently results in the fabrication of nano- and microstructured materials.

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REVIEW

Fabrication of nano- and microstructured chitin materials through gelation with suitable disperse media

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In this review, the recent development of the researches on the fabrication of nano- and microstructured chitin materials is presented, specifically focusing on approaches through its gelation with suitable disperse media. Although chitin is one of the most abundant natural polysaccharides on the earth, it is mostly an unutilized biomass resource due to lack of solubility and processability. For the efficient material production from chitin, the dissolution researches of chitin with proper solvent systems have been investigated including ionic liquids. For example, the author found that an ionic liquid, 1-ally-3-methylimidazolium bromide (AMIMBr), dissolved chitin in concentrations up to 5% (w/w) and additionally formed ion gels with the higher chitin contents. A highly concentrated $CaBr_2\square 2H_2O$/methanol was also found to induce the gelation with chitin. As one of the efficient nanomaterial production from chitin, self-assembled nanofibers have been fabricated by the regeneration from its solutions or gels with the appropriate solvents and disperse media according to bottom-up approach. For example, the chitin ion gel with AMIMBr was employed for the regeneration using methanol to produce a chitin nanofiber dispersion, which further constructed a film with a highly entangled nanofiber morphology by filtration. The physical and chemical approaches have been investigated to fabricate composite materials of the self-assembled chitin nanofibers with other polymeric components. As the former approach, for example, poly(vinyl alcohol) and carboxymethyl cellulose were compatibilized with the chitin nanofibers by means of co-regeneration and electrostatic interaction procedures, respectively. As the latter approach, surface-initiated graft polymerizations of some monomers from the chitin nanofiber films with the appropriate initiating groups have been conducted to obtain the composite films covalently linked to graft chains on the nanofibers. The regeneration from the gels with $CaBr_2\square 2H_2O$/methanol efficiently gave microporous materials.

Introduction

Natural polysaccharides are widely distributed in nature and regard as important vital materials for in vivo functions.[1] Of the many kinds of polysaccharides, cellulose and chitin are the representatively well-known and the most abundant organic substances on the earth. Both the polysaccharides act as structural materials in the cell walls of plants and the exoskeletons of crustaceans, shellfishes, and insects, respectively.[2-8] Accordingly, cellulose and chitin have the similar structures, in which the former is composed of β-(1→4)-linked D-glucose residues and the latter is an aminopolysaccharide consisting of *N*-acetyl-D-glucosamine units linked through β-(1→4)-glycosidic linkages (Fig. 1). Cellulose has been used for a number of traditional applications including its use in furniture, clothing, and medical products. Compared with cellulose, chitin still remains as an unutilized biomass resource, despite its huge production in nature and easy accessibility. The difficulty in the practical applications of chitin is mainly due to its intractable bulk structure and insolubility in water and common organic solvents. Furthermore, the chitin production from native resources involve complicated and harmful procedures including the treatments with strong acid and base because a native chitin from crustaceans, for example, has a fibrous structure that is arranged as microfibrils with proteins in the chitin–protein complexes, which assemble with minerals to construct exoskeletal shells of crustaceans.[9-11] Therefore, the chitin isolation requires the removal of mineral and protein constituents from the raw materials by the acid and base treatments. Because there is still major interest in conversion of chitin into various useful materials with controlled nano- and microstructures after the isolation from native resources and disentanglement of fibrils, considerable efforts have been

devoted to finding the solvent systems and disperse media of chitin for the efficient procedures on its dissolution and gelation.[7,12] Over the past decade, ionic liquids, which are low melting point salts that form liquids at temperatures below the boiling point of water, have been regarded as good solvents for polysaccharides such as cellulose[13-20] since Rogers et al. reported that an ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIMCl), dissolved cellulose in relatively high concentrations.[21] However, only the limited investigations have been reported regarding the dissolution of chitin with ionic liquids.[22-26] Accordingly, researches concerning the dissolution of chitin with proper ionic liquids have been being increasingly much attention to fabricate new chitin-based functional materials.

Fabrication of nanoscaled polymeric assemblies such as nanofibers and nanowhiskers, on the other hand, is one of the most variable methods to practically utilize polymeric compounds as material components, as observed in the case of cellulose.[27,28] For example, cellulose nanowhiskers have been used as reinforcing fillers for natural polymeric matrices.[29] The efficient approaches have also been developed for the fabrication of chitin nanofiber and nanowhiskers (nanocrystals).[7,12] Conventional approaches to the production of chitin nanofibers are mainly performed upon top-down procedures that break down the starting bulk materials from native chitin resources[30,31] because the native chitin microfibril is composed of nanofibers with 2-5 nm in width by the formation of crystalline structures among the chitin chains owing to numerous hydrogen bonds by hydroxy and acetamido groups (Figs. 2 and 3).[32,33] For the more detailed discussion on the chitin crystalline structures, three types of crystalline forms, i.e., α-, β-, and γ-chitins, are known depending on the arrangement of the polymeric chains (Fig. 1). The most abundant form is α-chitin (e.g., from crab and shrimp shells), where the polymeric chains are aligned in an antiparallel fashion.[34] This arrangement is favourable for the formation of strong intermolecular hydrogen bonding, leading to the most stable form in the three types of crystalline structures. In β-chitin (e.g., from squid pen), the polymeric chains are packed in a parallel arrangement, resulting in weaker intermolecular forces.[35] Accordingly, β-chitin is considered to be less stable than α-chitin. γ-Chitin may be a mixture of α- and β-forms. As the representative top-down approach for the fabrication of nanostructured chitin materials, the formation of nanoscaled chitin assemblies was reported by acid treatment of a native chitin resource.[36-39] Microfiller fragments of crab and shrimp chitins were prepared by hydrolysis in HCl aqueous solution (3 mol/L) at its boiling point. After removal of the acid by centrifugated washing and dialysis, ultrasonication converted the residual product into a colloidal suspension of crystallites (chitin nanowhiskers). As another top-down approach, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation of chitin in water at pH10 under specific conditions and subsequent ultrasonication were performed to fabricate chitin nanowhiskers and nanofibers dispersed in water.[40,41] A simple grinding technique has also been developed for the preparation of chitin nanofibers from chitin microfibrils.[42-45] The author recently reported that nanofibrillation of a native chitin powder was facilely achieved by N_2 gas bubbling with conventional ultrasonication in water.[46]

The other method for the fabrication of chitin nanostructures accorded to self-assembling generative (bottom-up) route, in which fibrillar nanostructures were produced by regeneration from chitin solutions or gels via appropriate processes, as examples of the electrospinning equipment[47,48] and simple precipitation process (Fig. 3).[49-53] The author also reported that self-assembled chitin nanofibers were facilely fabricated by regeneration from an ion gel of chitin with an ionic liquid using methanol, followed by ultrasonication.[12,26,31]

On the other hand, porous materials with controlled porosity in nano- and microscals have practically been used in applications such as adsorption and extraction.[54] Such porous structures generally constructed by reconstitution such as lyophilization after proper dissolution or gelation of polymeric components. Chitin microporous materials have also been prepared by suitable regeneration procedures from chitin solutions or gels with disperse media.[55,56]

In this review article, the recent development on the fabrication of nano- and microstructured chitin materials according to the regenerative bottom-up approach is presented, specifically focusing on approaches through the proper gelation with suitable disperse media. The solvent systems and disperse media for chitin including the ionic liquids are briefly reviewed at the first section. Then, the fabrication of self-assembled chitin nanofibers by regeneration technique mainly from a chitin ion gel with an ionic liquid is overviewed. Applications of nanostructured chitin to compatibilize with other polymeric components are also disclosed to produce chitin nanofiber composite materials. The facile production of chitin microporous materials by regeneration from gels with the disperse media is finally reviewed.

Dissolution and Gelation of Chitin

Chitin exhibits the limited affinity toward common solvents due to strong intermolecular hydrogen bonding and thus is not dissolved with conventional organic solvents and water. The most widely used solvent systems for chitin are 5-7% LiCl/*N,N*-dimethyladcetamide (DMAc)[57] and $CaCl_2\square 2H_2O$-saturated methanol.[58-61] Because LiCl forms a complex with chitin that is soluble in DMAc, 5-7% LiCl/DMAc mixtures are also possible to dissolve chitin. Tamura et al. reported that methanol saturated with $CaCl_2\square 2H_2O$ dissolved chitin in a few% concentrations at refluxed temperature although anhydrous $CaCl_2$ was not suitable for dissolution. Recently, the author reported that 0.9–3.5% (w/v) mixtures of chitin with highly concentrated $CaBr_2\square 2H_2O$/methanol (3.85 mol/L) formed gels by stirring at room temperature, whereas chloride analogue of this solution system did not induce the gelation with chitin at that temperature.[62]

The dissolution of chitin has also been reported using highly polar fluorinated solvents such as hexafluoroisopropyl alcohol (HPIP) and hexafluoroacetone sesquihydrate.[63-64] Strong protic acids such as trichloroacetic acid and dichloroacetic acid have been found to dissolve chitin.[65-67] Methanesulfonic acid was reported to from a colloidal chitin.[68] Interestingly, cold aqueous NaOH (16% (w/w)) was also found to dissolve chitin[69,70] and the produced alkali chitin exhibited the lower critical solution temperature.[71]

Some ionic liquids have been found to dissolve chitin (Fig. 4).[22-26] Over the past decade, ionic liquids have attracted much attention due to their specific characteristics such as excellent thermal stabilities, a negligible vapor pressure, and controllable physical and chemical properties.[72,73] The interests and applications on ionic liquids have also been extended to the researches related to biological macromolecules such as polysaccharides, because of specific good affinities of ionic liquids for them.[13] The dissolution behavior of chitin in a series

of alkylimidazolium chloride and dimethyl phosphate and 1-allyl-3-methylimidazolium acetate has been investigated.[22] Consequently, the former two series of the ionic liquids did not dissolve the certain amounts of chitin (less than 1.5 wt%), but the latter ionic liquid showed a ability for dissolution of chitin in 5 wt%. Furthermore, the dissolution behavior was affected by the degree of deacetylation, the degree of crystallinity, and the molecular weight. Besides, the following alkylimidazolium acetates, 1-butyl- and 1-ethyl-3-methylimidazolium acetates (BMIMOAc and EMIMOAc, respectively), have also been found to dissolve chitin in certain concentrations.[74,75] BMIMOAc dissolved both α- and β-chitins with different molecular weights at relatively lower temperature. Cooling the chitin/BMIMOAc solutions to ambient temperature resulted in corresponding chitin/BMIMOAc gels, which further formed chitin sponge and film materials by regeneration using water or methanol coagulant. Because it was also found that EMIMOAc dissolved chitin, extraction of chitin from raw crustacean shells, such as shrimp shell, was demonstrated using EMIMOAc.

The author also studied on the dissolution of chitin with ionic liquids. To discover the ionic liquids that dissolve chitin, the author has noted the previous study on synthesis of polyamides and polyimides using the ionic liquids with the imidazolium bromide structure as reaction media.[76] The investigation inspired to employ the same kind of ionic liquids for the dissolution of chitin because chitin forms strong hydrogen bonding by the –N-C=O groups of acetamido causing the solubility problem as same as the case of polyamides and polyimides. Accordingly, three imidazolium-type ionic liquids with bromide counter anion were prepared for the dissolution study, which were 1-allyl-3methylimidazolium, 1-methyl-3-propylimidazolium, and 1-butyl-3-methylimidazolium bromides (AMIMBr, MPIMBr, and BMIMBr, respectively).

For the dissolution study, a mixture of chitin with each ionic liquid was heated at 100 °C and the dissolution process was simply followed by observation using a charge coupled device (CCD) camera with 200 times magnification scale (Fig. 5(a)). When AMIMBr was used for the experiment, a clear solution of chitin was obtained in the concentrations up to ~5% (w/w) (Fig. 5(b)), whereas chitin powders were totally remained after the heating process of the mixture of chitin with MPIMBr or BMIMBr even in 3% (w/w) concentration (Figs. 5(c) and (d)).[77] These results indicated that only AMIMBr in the three ionic liquids with bromide counter anion employed showed an ability to dissolve chitin. The dissolution of chitin with AMIMBr was further confirmed by the SEM measurement. The SEM image of the mixture of chitin with AMIMBr (5% (w/w)) after heating at 100 °C for 48 h did not show any solid morphology, unlike that observed in the SEM image before heating (Figs. 6(a) and (b)), suggesting that 5% (w/w) chitin was solvated with AMIMBr.

Interestingly, gel-like materials (ion gels) with higher viscosity were formed when 7-12% (w/w) amounts of chitin were immersed in AMIMBr, followed by heating at 100 °C for 24 h and cooling to room temperature. Indeed, the resulting 7% (w/w) chitin with AMIMBr did not flow upon leaning a test tube, whereas the aforementioned 5% (w/w) solution of chitin with AMIMBr started to flow upon leaning (Figs. 6(c) and (d)). Although the dynamic rheological measurements showed that both 5 and 7% (w/w) chitins with AMIMBr behaved as the weak gels, the much lower yield stress of 5% (w/w) chitin with AMIMBr than that of 7% (w/w) system supported that the former can flow under gravitation.

The preparation of the chitin/cellulose composite ion gel using the two ionic liquids, AMIMBr and BMIMCl, was performed (Fig. 7)[78-80] because the author also reported the formation of an ion gel of cellulose with BMIMCl in the previous literature.[81] First, 5% (w/w) chitin and 10% (w/w) cellulose were dissolved in each appropriate ionic liquid, AMIMBr and BMIMCl, respectively. Then, the two solutions were mixed in the desired ratios at 100 °C to give the homogeneous mixtures. The gels were obtained by standing the mixtures at room temperature for 4 days. The resulting ion gels were characterized by the powder X-ray diffraction (XRD) and thermal gravimetrical analysis (TGA) measurements, which showed relatively good miscibility among the polysaccharides and ionic liquids in the materials. The mechanical properties of the gels were changed depending on the ratios of chitin to cellulose in the materials. The composite ion gels were further converted into chitin/cellulose composite films as followed (Fig. 7).[78,82] After the chitin/cellulose homogeneous mixtures with AMIMBr/BMIMCl prepared as above were casted on a glass plate and left standing at room temperature for 2 h, the obtained gel-like materials were subjected to successive Soxhlet extractions with ethanol for 12 h and with water for 12 h and dried to give the composite films.

The chitin/cellulose composite ion gel has been employed as the novel electrolyte for an electric double layer capacitor (EDLC).[83-85] First, the ion gel was treated with an aqueous 2.0 mol/L H_2SO_4 solution for 3 h to convert into an acidic gel. Electrochemical characteristics of the resulting acidic chitin/cellulose composite gel electrolyte were investigated by galvanostatic charge-discharge measurements. The test cell with the composite gel electrolyte exhibited a specific capacitance of 162 F/g at room temperature, which was higher than that for a cell with an H_2SO_4 electrolyte (155 F/g). Moreover, the discharge capacitance of the test cell retained over 80 % of its initial value in 10^5 cycles even at a high current density of 5000 mA/g. These results indicated that the acidic chitin/cellulose composite gel electrolyte had a practical applicability to an advanced EDLC with the excellent stability and working performance.

Fabrication of Self-assembled Chitin Nanofibers by Regenerations from Ion Gels

Self-assembled chitin nanofibers were fabricated from the solutions of chitin such as HFIP and LiCl/DMAc.[49-52] The self-assembling process was initiated through either solvent evaporation for the HFIP system or addition of water for the LiCl/DMAc system. Self-assembling of chitin was simply conducted, in which slowly drying of the former solutions in appropriate concentrations led to long (10-100 μm) nanofibers with a small diameter (ca. 2.8 nm). For the low volatility of the latter solution, simple drying approach was not suitable, whereas fibers were easily precipitated out upon addition of water. Nanofibers fabricated in this fashion had a larger diameter (ca. 10 nm) than those obtained from the HFIP system, while the lengths of both the nanofibers were comparable. Moreover, the nanofibers exhibited α-chitin crystalline structures.

An electrospinning method was used to fabricate self-assembled nanofibers.[47,48] Chitin was first depolymerized by γ-irradiation to improve its solubility. The electrospinning of the resulting chitin was then carried out with HFIP as a spinning solvent. The SEM images of nanofibers were seen from electrospun samples. At the concentrations of the HFIP

solutions up to 3 wt%, large irregular beads or beaded fibers were generated by electrospinning. The continuous nanofibers were fabricated at the concentrations more than 4 wt%, indicating that extensive chain entanglements were necessary to produce the continuous fibers of chitin by this approach. At 6 wt% concentration, however, the continuous and uniform process for electrospinning was inhibited because the solution had a very high viscosity. The resulting fibrous structure containing irregular, but small beads was observed. Although as-spun nanofibers had the broad diameter distribution, most of the fiber diameters were less than 100 nm.

The ionic liquid, AMIMBr, was also employed as the media for the fabrication of self-assembled chitin nanofibers by the regeneration approach (Fig. 8(a)).[86] A commercially available chitin powder from crab shells was first swollen with AMIMBr according to the procedure reported in the author's study as aforementioned to give chitin ion gels (10-12% (w/w)). When the gels were soaked in methanol at room temperature for 24 h to slowly regenerate chitin, followed by sonication, dispersions were obtained. The resulting dispersions were further diluted with methanol to subject to the SEM measurement for evaluation of the morphology of the regenerated chitin. Consequently, the SEM image of a sample from the dispersion showed the nanofiber morphology with ca. 20-60 nm in width and several hundred nm in length (Fig. 8(a)), indicating the self-assembling formation of the chitin nanofibers by the above regeneration approach from the ion gel. When the dispersion was subjected to filtration to isolate the nanofibers, the residue formed a film, which was further purified by Soxhlet extraction with methanol. The SEM image of the resulting film exhibited the pattern of highly entangled nanofibers (Fig. 8(a)). Such entangled structure from the nanofibers probably contributed to formability of the film. The XRD pattern of the nanofiber film mainly showed four diffraction peaks at around 9.5, 19.5, 20.9, and 23.4°, which typically corresponded to crystalline structure of α-chitin[87] and is identical with that of an original chitin powder from crab shells. This result indicated that the α-chitin crystalline structure was reconstructed during the formation of the nanofibers by the regeneration procedure.

In the following study, the author found that the morphologies of self-assembled chitin nanofibers were affected when the regeneration from the chitin ion gels were conducted using calcium halide□$2H_2O$/methanol solutions.[88] The regeneration from the ion gel using $CaCl_2$□$2H_2O$ or $CaBr_2$□$2H_2O$/methanol solution in high concentration did not induce the nanofiber assembly. Compared with the aforementioned regeneration using a sole methanol, on the other hand, the nanofibers with higher aspect ratio were produced by the regeneration process using $CaBr_2$□$2H_2O$/methanol solution in lower concentration. The mechanical property of the film formed by the filtration of the resulting dispersion was enhanced compared with the chitin nanofiber films obtained using the other methanolic solutions.

Preparation of Composite Materials from Self-assembled Chitin Nanofibers

As one of the possible applications of the self-assembled chitin nanofibers, attempts have been made to fabricate composite materials with other polymers. Two kinds of processes, that is, physical and chemical approaches, have been considered to produce the composite materials from nanofibers (Fig. 9).[12] In former case, nanofibers and polymer components are compatibilized by appropriate physical interactions, whereas the latter approach results in the formation of covalent linkages between nanofibers and polymers for compatibilization.

By the physical approach, for example, the self-assembled chitin nanofiber/poly(vinyl alcohol) (PVA) composite films were fabricated (Fig. 8(b)).[86] First, 10% (w/w) chitin ion gel with AMIMBr was prepared according to the aforementioned procedure and a solution of PVA (DP = ca. 4300) with a small amount of hot water was added to the gel (feed weight ratio of chitin to PVA = 1:0.3). Because methanol is a poor solvent for PVA, then, the co-regeneration of the two polymers was conducted by soaking the mixture in methanol, followed by filtration and Soxhlet extraction with methanol to produce the self-assembled chitin nanofiber/PVA composite film. The SEM image of the composite film showed the remaining of the nanofiber morphology (Fig. 8(b)). This result suggested that the two polymer components were relatively immiscible in the composite and the PVA components probably filled in spaces among the fibers. Indeed, the DSC profile of the film exhibited an endothermic peak assignable to the melting point of PVA, indicating the formation of crystalline structure separated from the chitin nanofibers because of the immiscibility. However, the melting point peak of PVA in the DSC curve of the film was broadened owing to decreasing the crystallinity. This data indicated that chitin and PVA might partially be miscible at the interfacial area on the fibers by hydrogen bonding between the two polymer components. Both the values of tensile strength and elongation at break of the composite film under tensile mode were larger than those of the chitin nanofiber film. This result supported that the presence of PVA components in the composite film contributed to enhancement of the mechanical property.

Because chitin can be considered as a basic polysaccharide owing to the presence of several% of free amino groups in total repeating units by deacetylation of acetamido groups, the self-assembled chitin nanofibers were used as reinforcing agent for an acidic polysaccharide, that is, carboxymethyl cellulose (CMC), by electrostatic interaction.[89] CMC is one of the most widely applied cellulose derivatives in detergent, food, paper, and textile industries and shows good processabilities such as the film formation.[90] For the compatibilization, the CMC films, which were prepared by casting technique, were immersed in the self-assembled chitin nanofiber dispersions with the different contents obtained by the aforementioned regeneration procedure from the ion gels (Fig. 10). After centrifugation, the resulting composite films were washed with methanol and drying. The amounts of the chitin nanofibers on the films increased with increasing the nanofiber contents in the dispersions. The SEM images of the films showed the nanofiber morphology on the films (Fig. 10). The reinforcing effect of the nanofibers present on the films was confirmed by tensile testing and the amounts of the nanofibers strongly affected enhancement of the mechanical property.

Chitin-based eco-friendly composite materials have previously been prepared by the physical compatibilization approach with aliphatic biodegradable and biocompatible polyesters[91-93] such as poly(L-lactide) (PLA) and poly(ε-caprolactone) (PCL).[94-97] Because such polyesters are facilely synthesized by ring-opening polymerization of the corresponding cyclic monomers, i.e., L-lactide (LA) and ε-caprolactone (CL), using alcohols as initiators in the presence of Lewis acid catalysts,[98,99] on the other hand, chemical grafting of the biodegradable polyesters by covalent linkages has also been performed by ring-opening polymerization approach using

chitin as a multifunctional initiator with a number of hydroxy (alcohol) groups.[100-103]

To obtain chitin nanofiber/biodegradable composite materials by the chemical approach, the author investigated surface-initiated ring-opening graft copolymerization of LA/CL initiated from hydroxy groups on the aforementioned self-assembled chitin nanofiber film (Fig. 11).[104] To efficiently initiate the copolymerization on surface of the nanofibers, spaces among the nanofibers were made by the aqueous treatment of the chitin nanofiber film. After the pre-treated film was immersed in a solution of the monomers, LA/CL (molar ratio = 20:80), in toluene, the surface-initiated ring-opening graft copolymerization was carried out in the presence of Lewis acid catalyst, tin(II) 2-ethylhexanoate, by heating the system at 80 °C for 48 h to give the chitin nanofiber-*graft*-poly(LA-*co*-CL) film. The IR spectrum of the resulting film supported the presence of the polyester in the product, which was explanatorily bound to the nanofibers by covalent linkage. The amount and the LA/CL compositional ratio of the grafted polyester were evaluated by the weight difference of the films before and after the grafting and the ^{1}H NMR analysis of the alkaline-hydrolysate, that is, the graft chains separated from the nanofibers by alkaline-treatment, to be 12.2% and 40/60, respectively. The LA/CL compositional ratio was higher than that in the feed because of the higher polymerizability of LA than CL.[105] The SEM image of the resulting composite film exhibited to remain the nanofiber morphology, but increase the fiber widths (60-100 nm) (Fig. 12(a)). Furthermore, some nanofibers were merged at the interfacial areas, that was probably caused by the grafted polyesters. The stress-strain curve of the composite film under tensile mode supported the enhancement of the mechanical property compared with the original chitin nanofiber film.

To provide further useful self-assembled chitin nanofiber-based composite materials, the surface-initiated grafting technique from the chitin nanofiber film was extended to employ a synthetic polypeptide as another biocompatible polymer. Because it has been well-known that synthetic polypeptides with well-defined structures are synthesized by ring-opening polymerization of α-amino acid *N*-carboxyanhydrides (NCAs) accompanied with decarboxylation initiated from amino groups,[106,107] the author investigated the surface-initiated graft polymerization of a NCA monomer from the chitin nanofiber film having amino initiating groups to give the chitin nanofiber-*graft*-polypeptide film.[108] As the monomer, moreover, γ-benzyl L-glutamate-NCA (BLG-NCA) was selected because its ring-opening polymerization and subsequent hydrolysis of ester linkages had given poly(L-glutamic acid) (polyGA) having free carboxylic acid groups. Because the ring-opening polymerization of the NCA monomer has been initiated with an amino group as aforementioned, deacetylation of acetamido groups in the chitin nanofiber film was conducted by the treatment with 40 % (w/v) NaOH aq. at 80 °C for 7 h to produce a partially deacetylated chitin (PDA-chitin) nanofiber film.[109] The degree of deacetylation of the product was estimated by the ratio of the absorption due to amido II at 1560 cm^{-1} to that due to the C–O stretching at 1070 cm^{-1} in the IR spectrum to be ca. 24 %. The SEM image and the XRD pattern of the resulting film were comparable to those before the alkaline treatment, suggesting the remaining of the nanofiber morphology and the crystalline structure, respectively. Then, the resulting PDA-chitin nanofiber film was immersed in a solution of BLG-NCA (20 equiv. for an amino group) in ethyl acetate at 0 °C for 24 h to occur the surface-initiated graft polymerization from amino groups. In the IR spectrum of the obtained the chitin nanofiber-*graft*-polyBLG film showed the C=O absorption due to ester linkage at 1735 cm^{-1}, strongly suggesting the presence of polyBLG in the product, which was explanatorily bound to the nanofibers by covalent linkage. The grafting amount of the polyBLG chains was evaluated by the weight difference of the films before and after the graft polymerization to be 18 wt%. The SEM image of the composite film indicated that the nanofiber morphology was still remained, but some fibers were merged at the interfacial areas (Fig. 12(b)), as well as that of the aforementioned chitin nanofiber-*graft*-poly(LA-*co*-CL) film.

Furthermore, the author found that a highly flexible chitin nanofiber-*graft*-polyGA network film was obtained by alkaline hydrolysis of ester linkages in the polyBLG chains on the composite film, followed by condensation of the produced sodium carboxylate groups with amino groups present in the film. First, the composite film was immersed in 1.0 mol/L NaOH aq. at 60 °C for 5 h for the alkaline hydrolysis of benzyl esters to convert into the chitin nanofiber-*graft*-polyGA film having sodium carboxylate groups. The IR spectrum of the film after the alkaline treatment supported the complete cleavage of benzyl esters to convert into sodium carboxylate groups. Then, the condensation of the resulting carboxylate groups with amino groups at the terminal end of the polyGA chains or those remaining on the nanofibers, which were not participated into the initiation of the graft polymerization, was conducted using the *N*-hydroxysuccinimide/water-soluble carbodiimide condensing agent in water at room temperature for 12 h to construct polyGA/chitin networks in the film. The intensity ratio of the amido II absorption to the C-O stretching absorption in the IR spectrum of the product was 22 % larger than that of the film before the condensation. This result indicated the progress of the desired condensation reaction to yield the chitin nanofiber-*graft*-polyGA network film. The nanofiber morphology was seen in the SEM result of the produced film (Fig. 12(c)). The stress-strain curve of the resulting network film under tensile mode showed the lager elongation value at break than that of the original chitin nanofiber film with the comparable tensile strength values, indicating the more elastic nature of the former film. Indeed, the chitin nanofiber-*graft*-polyGA network film had the highly flexible nature, in which this was bended without breaking.

The author also investigated surface-initiated atom transfer radical polymerization (ATRP) from a chitin nanofiber macroinitiator film. ATRP is a versatile technique to control the chain length and polydispersity of the resulting polymers and has been used to practically synthesize a wide range of polymeric materials with the designed structures.[110,111] Because ATPR is initiated from α-haloalkylacyl groups, the author synthesized the chitin macroinitiator with these initiating groups by esterification of hydroxy groups in chitin with the α-haloalkylacyl bromide, which was further used for the grafting of styrene by ATRP.[112]

On the basis of this previous study, the author synthesized the chitin nanofiber macroinitiator film for ATRP by the reaction of hydroxy groups on surface of the nanofibers with α-bromoisobutyryl bromide (30 equiv. for a repeating unit of chitin) in DMAc (Fig. 13).[113] The degree of substitution was calculated by the SEM-EDX measurement to be 0.61 for a repeating unit. Then, the surface-initiated ATRP of 2-hydroxyethyl acrylate (HEA) (20 eqiuv. for an initiating site) from the macroinitiator film was performed in the presence of CuBr/2,2'-bipyridine in 3 wt% LiCl/DMAc at 60 °C (Fig.

13).[112] The conversions of HEA were estimated by the weight differences of the films before and after ATRP, which increased with increasing the reaction times. The intensity ratio of the ester C=O absorption to the amido C=O absorption in the IR spectra of the products increased compared with those of the macroinitiator film, suggesting the progress of the graft polymerization. For the gel permeation chromatographic (GPC) measurement of the grafted polymer, the grafted polyHEA chains were separated from the produced composite films by alkaline hydrolysis to give poly(acrylic acid)s, which was further converted into poly(methyl acrylate)s by methyl esterification. The GPC peaks of the obtained poly(methyl acrylate)s shifted to higher molecular weight region with increasing the reaction times and their polydispersities were relatively narrow. These GPC results strongly supported that the longer polyHEA chains were grafted on the chitin nanofiber films by the gradual progress of ATRP with prolonged reaction times by living polymerization manner. In the SEM image of the composite film resulted by the lower monomer conversion (6%, polymerization time; 3 h), the nanofiber morphology was seen, but the average fiber width increased compared with that of the macroinitiator film (20 and 40 nm, Figs. 14(a) and (b), respectively). The SEM image of the composite film obtained by the higher monomer conversion (62%, polymerization time; 12 h) did not show the nanofiber morphology (Fig. 14(c)), indicating that the nanofibers were covered by the longer graft polyHEA chains. The stress-strain curves of the composite films under tensile mode obviously showed the larger values of elongation at break compared with those of the original chitin nanofiber film. Furthermore, the values of elongation at break increased with increasing the monomer conversions, whereas the tensile strength values decreased in this order. These data suggested the effect on enhancement of the flexibility by the grafting the longer polyHEA chains on the chitin nanofiber films.

Fabrication of Microporous Chitins through Gelation with Suitable Disperse Media

Microporous chitins have previously been fabricated by the appropriate regeneration approaches mostly via multiple steps from chitin solutions with some solvent systems. For example, a series of microporous chitins were obtained by freezing and lyophilization of chitin hydrogels, which were prepared by soaking the 0.2 – 2.0% chitin solutions with 5% LiCl/DMAc solvent system.[55] By subjecting the chitin hydrogels to the dry-ice/acetone cooling, the resulting porous chitins gave pore sizes measuring 200-500 μm. The smaller pore sizes, i.e., 100-200 μm were obtained when the chitin gels were frozen by liquid nitrogen and 10 μm pores were produced when the gels were placed in a freezer for 20 min.

The microporous chitins were also fabricated by lyophilization of the hydrogels, which were prepared by dialysis of the chitin solutions with saturated $CaCl_2\square 2H_2O$/methanol solution.[114,115] The regeneration from the solutions of chitin with BMIMOAc using ethanol, followed by Soxhlet extraction with ethanol and successive steps of supercritical drying (CO_2) gave microporous chitins.[116]

As aforementioned, the use of $CaBr_2\square 2H_2O$/methanol solution with moderate concentrations affected the regeneration process from the chitin ion gel, resulting in the production of chitin nanofibers with higher aspect ratios. This result inspired the specific affinity of $CaBr_2\square 2H_2O$/methanol solution toward chitin. Indeed, the author found that chitin gels were facilely obtained by stirring mixtures of chitin with highly concentrated $CaBr_2\square 2H_2O$/methanol solutions at room temperature, which were subsequently converted into microporous chtins (Fig. 15).[62] Because chitin has not been swollen by the same procedure using the saturated $CaCl_2\square 2H_2O$/methanol solution at room temperature, it can be noted that the swelling of chitin with the $CaBr_2\square 2H_2O$/methanol solution is specific behaviour. As a typical gelation procedure, when the mixtures of chitin (0.9 – 3.5% (w/v)) with 3.85 mol/L $CaBr_2\square 2H_2O$/methanol solution were stirred at room temperature, chitin was gradually swollen, leading to a gelling form after 48 h. The mixtures of chitin (1.8 (w/v)) with $CaBr_2\square 2H_2O$/methanol solutions in different concentrations also turned into a gelling form by the same procedure. The dynamic viscoelastic measurement of the resulting chitin gels suggested gelling state. Then, microporous chitins were efficiently fabricated by removing methanol from the gels under reduced pressure, followed by washing out $CaBr_2$ by water and subsequent lyophilization (Fig. 15).[62] The XRD profiles of the products indicated the construction of the α-chitin crystalline structure during the above regeneration procedure. The SEM measurement of the products supported the microporous morphology. Furthermore, it was found from the SEM results that porosities were depending on contents of chitin in the gels (Fig. 16). The mechanical properties of the microporous chitins under compressive mode were affected by the pore sizes. On the other hand, the amounts of $CaBr_2\square 2H_2O$ in the gels did not affect the porosities and mechanical properties of the microporous chitins.

Conclusions

In this article, the author reviewed the recent development of the researches on the fabrication of chitin nano- and micromaterials, mainly through gelation with suitable disperse media. Especially, the most of the present review has spent to concern with the author's studies on this research topic. A variety of solvent systems and disperse media for chitin have increasingly been found, which lead to the efficient material production from chitin. For example, the chitin nanofibers and microporous materials were facilely fabricated by the regeneration technique from the gels with the suitable disperse media. The ionic liquids are one of the highly potential solvent and disperse media for chitin, and thus, the author found that the self-assembled chitin nanofibers were obtained by the regeneration from the ion gels. Furthermore, the composite materials of the chitin nanofibers with other polymeric components have been constructed by both the physical and chemical approaches.

Chitin is one of the most abundant natural polysaccharide and can absolutely be expected to be used as the material component even compared with cellulose owing to its biocompatibility. Because the studies on the fabrication of chitin materials have significantly been developed as representatively appeared in this review, the further practical chitin materials will be fabricated and employed in the application fields related to medicinal, pharmaceutical, and environmental industries in the future.

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Notes and references

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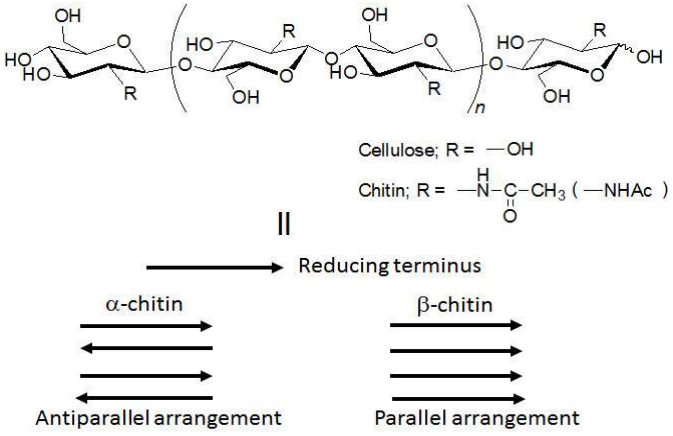

Fig. 1 Chemical structures of cellulose and chitin and image for crystalline structures of chitin.

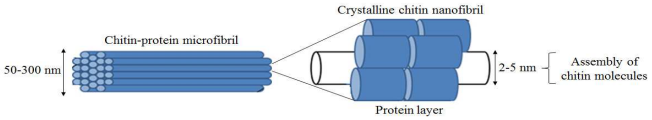

Fig. 2 Image for hierarchically ordered assemblies of native chitin.

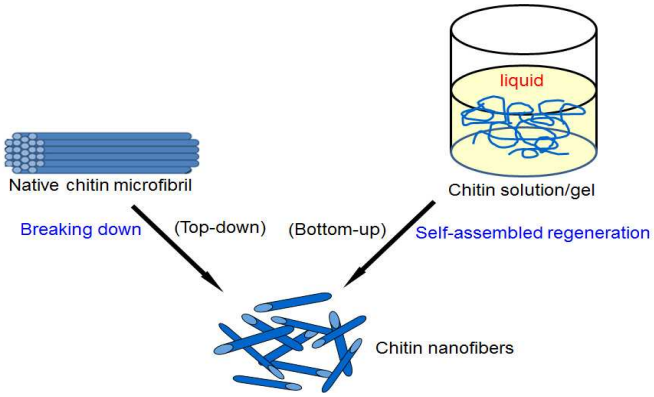

Fig. 3 Top-down and bottom-up approaches for fabrication of chitin nanofibers.

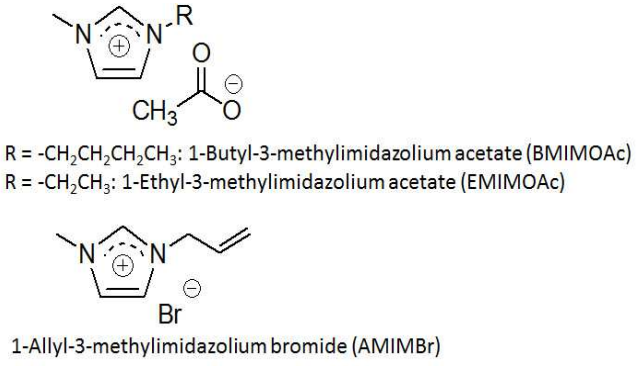

Fig. 4 Representative ionic liquids that dissolve chitin.

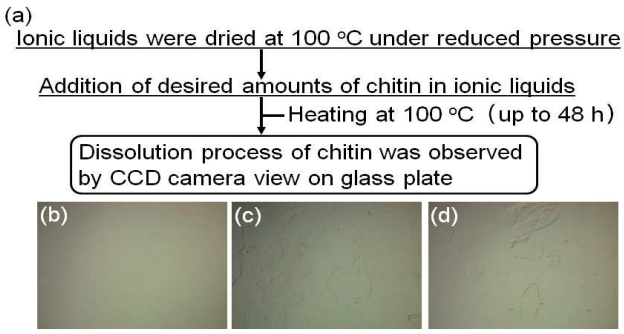

Fig. 5 Procedure for dissolution experiment of chitin with ionic liquids (a) and CCD camera view of dissolution experiment mixtures after heating at 100 °C for 48 h; 5% (w/w) with AMIMBr (b), 3% (w/w) with MPIMBr (c), 3% (w/w) with BMIMBr (d).

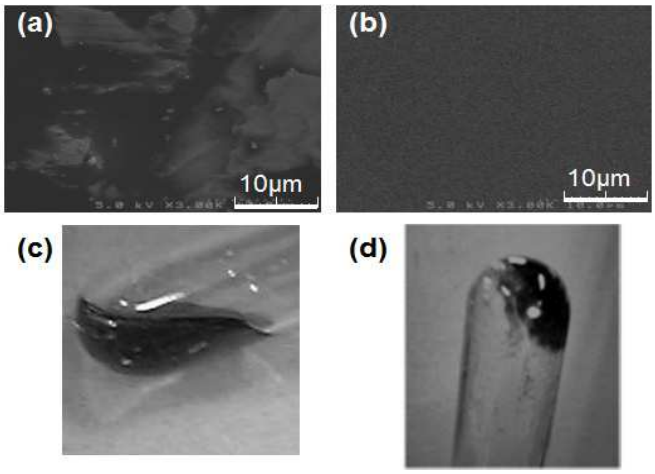

Fig. 6 SEM images of mixtures of chitin with AMIMBr (5% (w/w)) before and after dissolution experiment (a and b) and photographs of 5% (w/w) liquid (c) and 7% (w/w) gel (d) of chitin with AMIMBr after heating at 100 °C for 48 h.

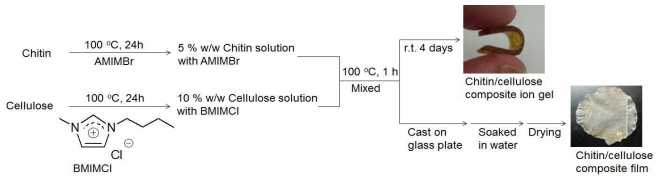

Fig. 7 Preparation procedures of chitin/cellulose composite gel and film.

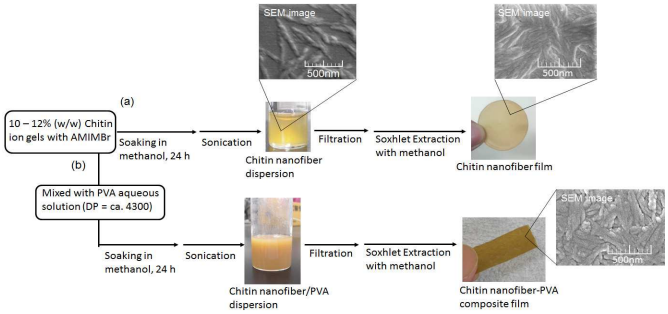

Fig. 8 Preparation procedures of chitin nanofiber dispersion and film (a), chitin nanofiber/PVA composite film (b), and their SEM images.

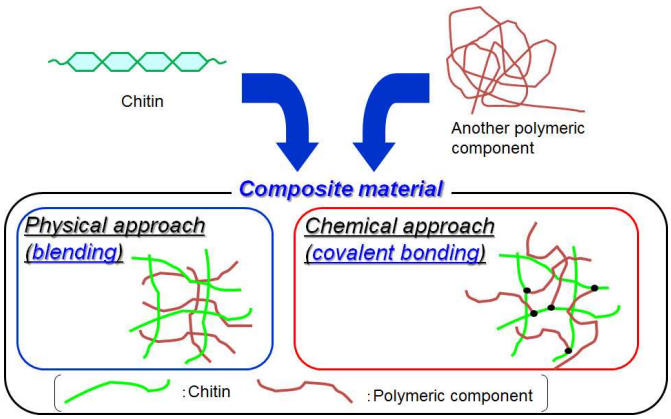

Fig. 9 Physical and chemical approaches for preparation of composite materials of chitin with another polymeric component.

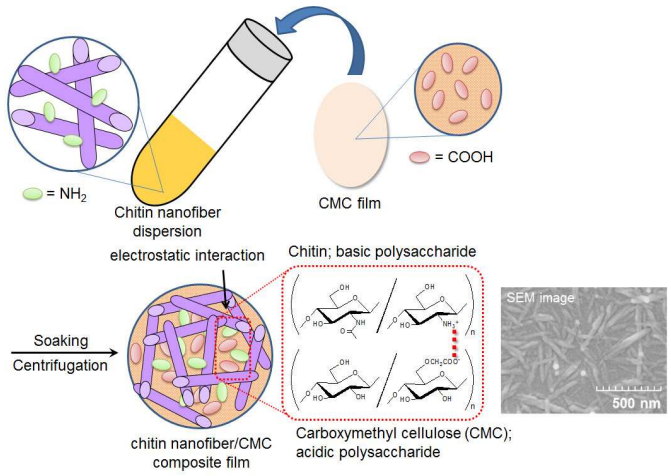

Fig. 10 Preparation procedure of chitin nanofiber/CMC composite film and its SEM image.

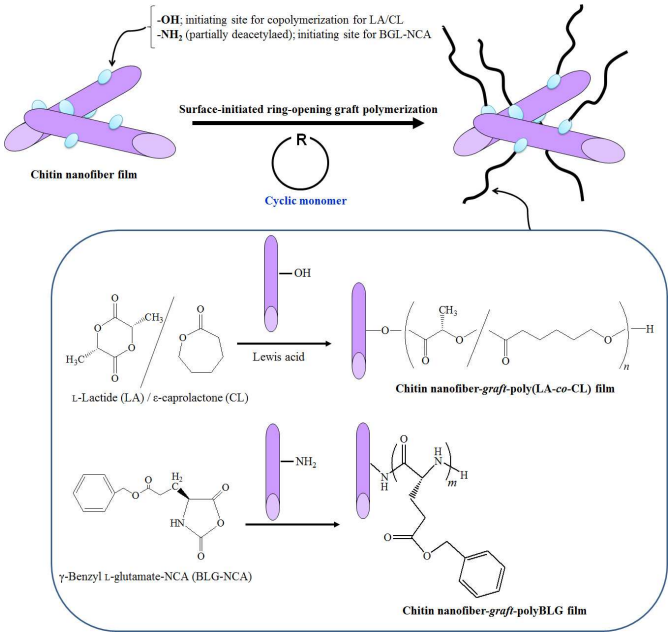

Fig. 11 Surface-initiated ring-opening graft (co)polymerization of LA/CL and BLG-NCA from chitin nanofiber film.

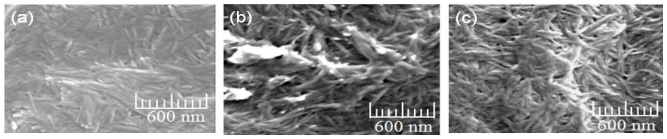

Fig. 12 SEM images of chitin nanofiber-*graft*-poly(LA-*co*-CL) film (a), chitin nanofiber-*graft*-polyBLG film, and chitin nanofiber-*graft*-polyGA network film (c).

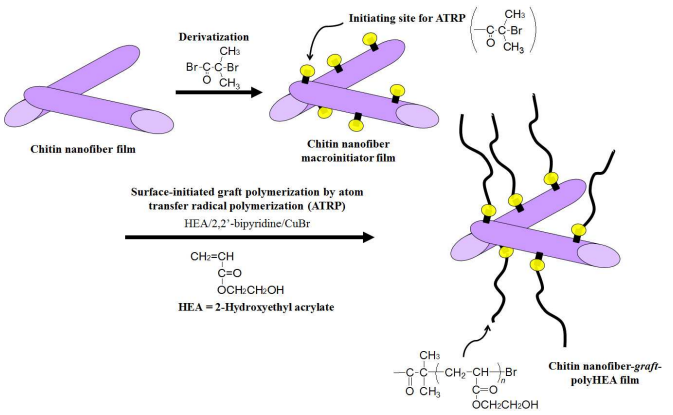

Fig. 13 Synthesis of chitin nanofiber macroinitiator film and surface-initiated graft ATRP of HEA.

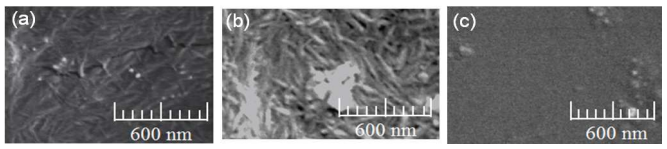

Fig. 14 SEM images of chitin nanofiber macroinitiator film (a) and chitin nanofiber-*graft*-polyHEA films obtained by the reaction times of 3 and 12 h (b and c, respectively).

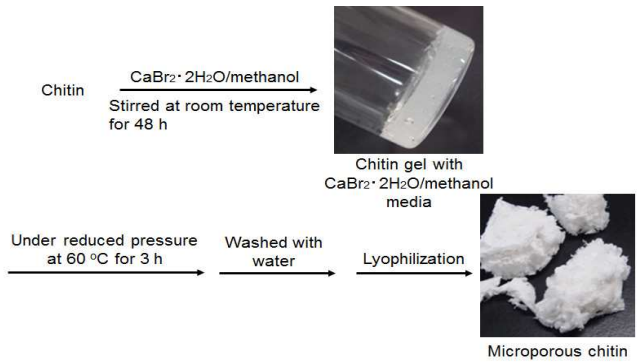

Fig. 15 Preparation procedures of chitin gel with $CaBr_2 \square 2H_2O$/methanol media and microporous chitin.

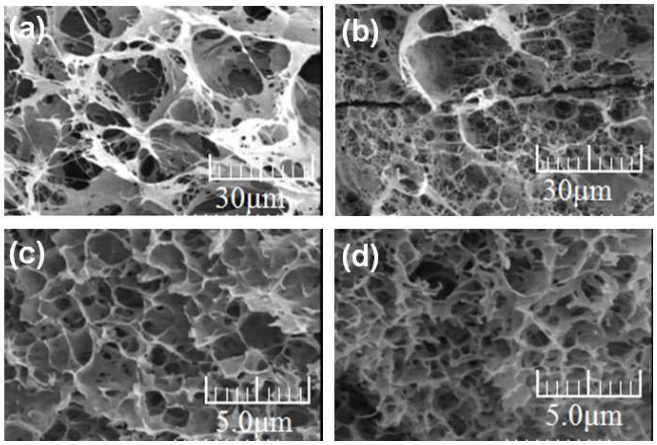

Fig. 16 SEM images of microporous chitins obtained from 0.9, 1.8, 2.4, and 3.5% (w/v) chitin gels with 3.85 mol/L $CaBr_2 \square 2H_2O$/methanol media ((a), (b), (c), and (d), respectively).

Jun-ichi Kadokawa studied applied and materials chemistries at Tohoku University, where he received his Ph.D. in 1992. He then joined Yamagata University as a Research Associate. From 1996 to 1997, he worked as a visiting scientist at the Max-Planck-Institute for Polymer Research in Germany. In 1999, he became an Associate Professor at Yamagata University and moved to Tohoku University in 2002. He was appointed as a Professor of Kagoshima University in 2004. His research interests focus on nanostructured polysaccharide materials. He received the Award for Encouragement of Research in Polymer Science (1997) and the Cellulose Society of Japan Award (2009).