

## Preparation of pectin-inorganic composite material as accumulative material of metal ions

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**ABSTRACT:** Pectin is one of the biopolymers in the cell walls of all plant tissues, but the pectin-containing materials have been discarded as industrial waste in food-processing factories. We prepared a water-insoluble pectin-inorganic composite material by mixing pectin and a silane coupling reagent, bis(3-trimethoxysilylpropyl)amine. The mechanical strength of the pectin-inorganic composite material was higher than that of the pectin material without the addition of an inorganic component. In addition, the thermal stability of the composite material increased with the addition of the inorganic component. Furthermore, when the pectin-inorganic composite materials were incubated in an aqueous solution of Cu(II), Zn(II), or In(III), these composite materials effectively accumulated not only the heavy metal ions, but also rare-earth metal ions. Additionally, based on the infrared (IR) measurements, the metal ion accumulative mechanism into the composite material is described. As a result, the IR spectra suggested an electrostatic interaction between the metal ion and carboxy group in the pectin. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, 132, 42056.

**KEYWORDS:** applications; bioengineering; biopolymers and renewable polymers; composites; polysaccharides

Received 28 October 2014; accepted 28 January 2015

DOI: 10.1002/app.42056

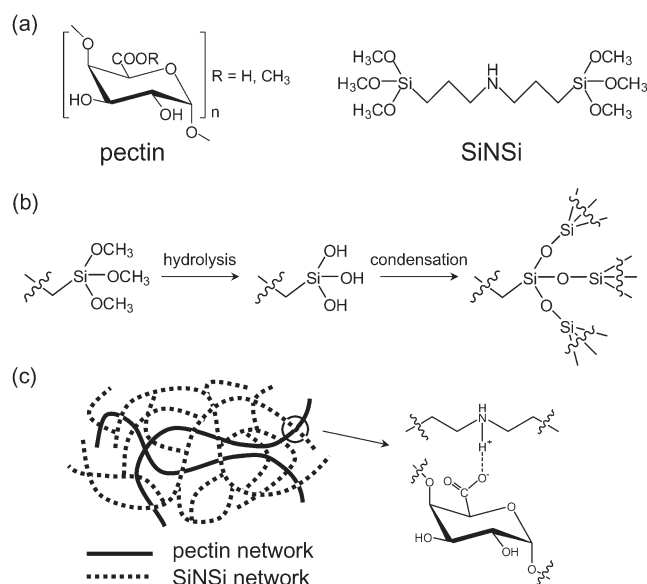
### INTRODUCTION

Pectin, one of the natural polysaccharides, widely occurs in plants, particularly in fruits and young tissues.<sup>1,2</sup> The chief commercial sources are the peel of various citrus fruits and apple pomace, and these materials have been discarded as industrial waste in food-processing factories around the world.<sup>3</sup> Additionally, pectin is a nontoxic, biodegradable, and water-soluble material.<sup>1,2</sup> Therefore, pectin or pectin-containing materials have been used as a gelatinizing agent in foods. Furthermore, pectin mainly consists of  $\alpha$ (1-4)-linked D-galacturonic acid, and this carboxy group can strongly interact with the metal ions, such as heavy metal and alkaline earth metal ions.<sup>4,5</sup> These properties, such as a strong interaction with metal ions, have been used as the ion-exchange and removal materials of metal ions.<sup>6-10</sup> However, as the pectin does not have a mechanical strength, the pectin-containing material cannot be used for a long time under environmental and practical conditions. Therefore, for utilization of pectin as an absorbent of metal ions, the preparation of a pectin material with the required mechanical strength is necessary.

The organic-inorganic composite materials have become attracted as functional materials.<sup>11-14</sup> These organic-inorganic composite materials have both the properties of the flexibility of an organic material and the mechanical strength of an inorganic material.<sup>11-15</sup> In addition, as the organic-inorganic composite

materials are synthesized by a soft process, such as the sol-gel synthesis, these techniques can apply to various organic molecules, such as dye molecules, proton conductive molecules, polymers, and so forth. Especially, the organic-inorganic composite material with a biological substrate, such as a protein, polysaccharides, and nucleic acid, is a novel material with a biological function.<sup>14,16-20</sup> Therefore, the organic-inorganic composite materials with a biological substrate have been reported to be an absorbent of carcinogenic molecules and endocrine disruptors,<sup>20-22</sup> energy materials,<sup>23</sup> the removal material of heavy metal ions,<sup>24,25</sup> the sensing material of biological molecules,<sup>18,26</sup> column materials for liquid chromatography,<sup>19,27</sup> and biomaterials.<sup>18,28</sup> However, the accumulation of rare-earth ion from aqueous solution by the pectin-inorganic composite material has not been reported as far as we know.

In this study, we prepared the water-insoluble pectin-inorganic composite material by mixing pectin and, a silane coupling reagent, bis(3-trimethoxysilylpropyl)amine. The mechanical strength of the pectin-inorganic composite material was higher than that of the pectin material without the addition of an inorganic component. In addition, we demonstrated the accumulation of metal ions by the composite material. When the pectin-inorganic composite materials were incubated in a metal ion-containing aqueous solution of rare-earth ions, these composite materials effectively accumulated the metal ions. Furthermore,



**Scheme 1.** (a) Molecular structure of pectin and bis(trimethoxysilyl)propylamine (SiNSi). (b) Condensation reaction of SiNSi. (c) Structural model of pectin-SiNSi composite material with the cross-linking between SiNSi and pectin by the electrostatic interaction.

we obtained infrared (IR) measurements in order to discuss the accumulative mechanism of the metal ions into the composite material. As a result, the IR spectra showed the electrostatic interaction between the metal ions and carboxy group in the pectin.

## EXPERIMENTAL

### Material

Pectin (from citrus, molecular weight  $2 \times 10^5$ – $3 \times 10^5$ ) was purchased from Wako Pure Chemical Industries, Osaka, Japan. The silane coupling reagent, bis[3-(trimethoxysilyl)propyl]amine (SiNSi), was purchased from Tokyo Kasei Industries, Tokyo, Japan. The molecular structures of pectin and SiNSi are shown in Scheme 1(a). Copper(II) chloride, zinc(II) chloride, chromium(III) chloride, yttrium(III) chloride, lanthanum(III) chloride, indium(III) chloride, aluminum chloride, calcium chloride, magnesium chloride, xylenol orange (XO), and methylthymol blue (MTB) were obtained from Wako Pure Chemical Industries, Kanto Chemical Co., Tokyo, Japan, or Dojindo Co., Kumamoto, Japan. Analytical grade solvents were used in all of the experiments described. Ultrapure water (Merck KGaA, Darmstadt, Germany) was used in this experiment.

### Preparation of Pectin-SiNSi Composite Material

Pectin-SiNSi composite material was prepared as follows: pectin aqueous solution (1 mL, 30 mg/mL) and 1M hydrochloric acid (50  $\mu$ L) was mixed in microtube. Further, SiNSi solution (0–114  $\mu$ L) was added in mixed solution and immediately mixed by the vortex mixer. This pectin-SiNSi mixed solution (100  $\mu$ L) was cast onto Teflon<sup>®</sup> plate and dried at room temperature overnight. These dried-composite films were stripped from the Teflon<sup>®</sup> plate, washed by water, and then stored in water. The

mixing ratio (wt %) of pectin and SiNSi was determined by eq. (1)

$$\text{wt \%} = \frac{[\text{weight of SiNSi}]}{[\text{weight of pectin}] + [\text{weight of SiNSi}]} \times 100 \quad (1)$$

where [weight of pectin] and [weight of SiNSi] of eq. (1) are weight of pectin and SiNSi in microtube, respectively. The mixing ratio of pectin and SiNSi was changed from 0–80 wt % (0–114  $\mu$ L).

The water stability in an aqueous solution of pectin-SiNSi composite material was confirmed by the following method: the five composite materials was immersed into 20 mL of pure water, 100 mM NaCl solution, 100 mM KCl solution, or 100 mM MgCl<sub>2</sub> solution at room temperature for 1 week. These composite materials was taken off from the solution, rinsed with water, and then dried at room temperature for 1 day. The amount of eluted composite materials was determined by the weight analysis before and after immersion into solution.

### Structural and Thermal Analyses of Pectin-SiNSi Composite Material

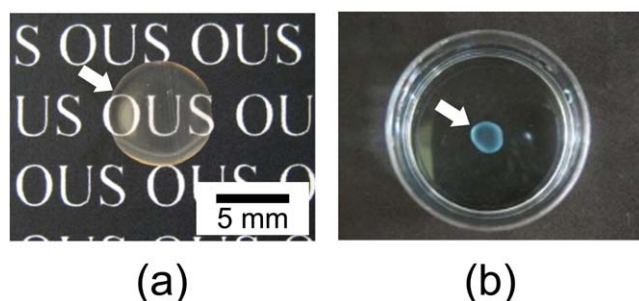
The IR absorption spectra of pectin-SiNSi composite material were measured by the KBr method using a FT-IR 8400 Fourier transform IR spectrometer (Shimadzu Corp., Kyoto, Japan). The IR spectrum was measured with the resolution of 4  $\text{cm}^{-1}$ . The thermal stability of the pectin-SiNSi composite material was analyzed by thermogravimetric-differential thermal analysis (TG-DTA) (DTG-60, Shimadzu Corp.). The TG-DTA measurement was carried out at a heating rate of 10°C min<sup>-1</sup> under a dry-nitrogen flow. Sample weights of TG-DTA measurements were normalized at 1 mg.

### Tensile Strength of Pectin-SiNSi Composite Material

The pectin-SiNSi composite film was cut into 5 × 15 mm<sup>2</sup>. The thickness of composite film was measured by the thickness gauge ID-C X series (Mitutoyo Corporation, Kanagawa, Japan). The thickness of film was 70  $\mu$ m. The tensile stress and strain was measured using digital force gauge ZTA-50N (Imada CO., Aichi, Japan) and test stand MX2-500N (Imada CO.). The temperature and relative humidity at the tensile strength measurements were 25°C and 50 ± 5%, respectively. The initial length of the composite film was 5 mm and the drawing speed was 10 mm min<sup>-1</sup>. The values of tensile stress and strain were expressed as an average of five measurements.

### Accumulation of Metal Ion by Pectin-SiNSi Composite Material

The copper(II) chloride, zinc(II) chloride, chromium(III) chloride, yttrium(III) chloride, lanthanum(III) chloride, indium(III) chloride, aluminum chloride, calcium chloride, and magnesium chloride were dissolved in pure water. The concentrations of aqueous metal ion solution were 0–100 ppm. The accumulation of metal ion by pectin-SiNSi composite material was demonstrated as follows: one pectin-SiNSi composite film was added into metal ion-containing aqueous solution, this solution was stirred at room temperature for 6 h, and then the composite film was separated from the aqueous solution. The accumulated amount of metal ion was determined by the absorbance of the aqueous solutions in the absence or presence of the pectin-



**Figure 1.** Photograph of pectin-30 wt % SiNSi composite material. (a) Dried composite material. (b) Cu(II)-accumulated composite material in an aqueous solution. Each arrows indicate the composite materials. The thickness of these composite materials under a dried condition was approximately 70  $\mu\text{m}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

SiNSi composite material. The concentration of aqueous metal ion solution was estimated from the calibration curve with the metal indicator XO and MTB.<sup>24,29,30</sup>

#### IR Measurements of Metal Ion-Accumulated Pectin-SiNSi Composite Material

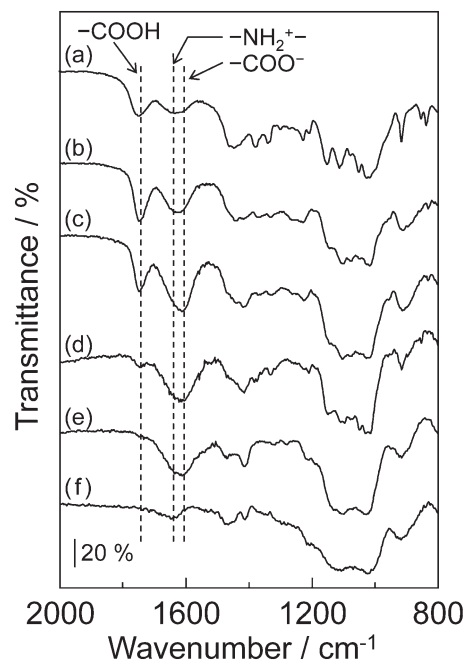
The metal ion-accumulated pectin-SiNSi composite materials were prepared by the incubation of composite film into metal ion-containing aqueous solution with various concentrations for 24 h. These metal ion-accumulated composite films were washed by pure water (50 mL  $\times$  3 times) and dried at room temperature overnight. These samples were analyzed by the KBr method using an IR spectrometer.

## RESULTS AND DISCUSSION

#### Preparation of Pectin-SiNSi Composite Material

The pectin-SiNSi composite material was prepared by mixing of the pectin and silane coupling reagent, bis(trimethoxysilylpropyl)amine (SiNSi). The mixing ratio of the pectin and SiNSi was varied from 0–80 wt %. Figure 1(a) shows a photograph of the dried pectin-30 wt % SiNSi composite film. The thickness of this composite film was approximately 70  $\mu\text{m}$ . This composite film was a transparent and flexible material and had the properties of an organic component. With the addition of  $\geq 50$  wt % SiNSi, the composite material did not produce the film with a good flexibility. Especially, the pectin-80 wt % SiNSi composite material produced a glass-like material. Therefore, in our research, we used the pectin-SiNSi composite material with the addition of 30 wt % SiNSi.

We next estimated the water-stability of the pectin-SiNSi composite material. Although the pectin material without the addition of the inorganic component was easily dissolved in water, the pectin-SiNSi composite material was not dissolved. Therefore, we measured the amount of eluted composite material by the weight analysis before and after immersion into solution. As a result, the amount of eluted composite material with the immersion in water for 1 week was about 0.2%. Additionally, we determined the effects of various salts on the elution of composite material. Although the composite materials were immersed at 100 mM NaCl solution, 100 mM KCl solution, or 100 mM  $\text{MgCl}_2$  solution for 1 week, the amounts of eluted



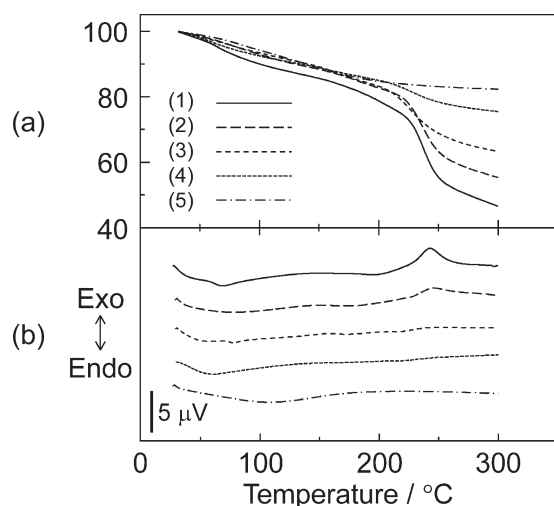
**Figure 2.** IR spectra of (a) pectin without the addition of SiNSi, (b) pectin-10 wt % SiNSi composite, (c) pectin-30 wt % SiNSi composite, (d) pectin-50 wt % SiNSi composite, (e) pectin-80 wt % SiNSi composite, and (f) dried SiNSi materials. The IR spectrum was measured at the resolution of 4  $\text{cm}^{-1}$ . Triplicate experiments gave similar results.

composite material were 4.0, 1.2, or 1.2%, respectively. These results suggested that the addition of the inorganic component, such as the silane coupling reagent, SiNSi, provided a water-stability to the pectin material. In addition, the pectin material with the addition of the inorganic component was stable in metal ion-containing aqueous solution.

#### Composite Structure of Pectin-SiNSi Composite Material

Figure 2 shows the IR spectra of (a) pectin without the addition of SiNSi, (b) pectin-10 wt % SiNSi composite, (c) pectin-30 wt % SiNSi composite, (d) pectin-50 wt % SiNSi composite, (e) pectin-80 wt % SiNSi composite, and (f) dried SiNSi materials. The absorption band of the C=O stretching vibration<sup>4,31–33</sup> of in the  $-\text{COOH}$  group of the pectin molecule at  $1743\text{ cm}^{-1}$  almost disappeared by the addition of the SiNSi molecule. In addition, the absorption band at  $1597\text{ cm}^{-1}$ , related to the symmetric stretching vibration of  $-\text{COO}^-$ ,<sup>4,31–33</sup> relatively increased when the SiNSi molecule was added to the pectin molecule. These results suggested that the  $-\text{COOH}$  group became deprotonated by the addition of the SiNSi molecule and formed the  $-\text{COO}^-$  group. In contrast, the absorption band at  $1643\text{ cm}^{-1}$ , attributed to the symmetric stretching vibration of the secondary ammonium salt,<sup>31</sup> relatively increased with the addition of the pectin molecule. These phenomena suggested that the  $-\text{NH}-$  group of the SiNSi molecule formed the  $-\text{NH}_2^+-$  group by the proton from the  $-\text{COOH}$  group and the pectin-SiNSi composite material had been formed by the electrostatic interaction between the  $-\text{COO}^-$  group of the pectin molecule and  $-\text{NH}_2^+-$  group of the SiNSi molecule.

On the other hand, in the pectin-SiNSi composite material, the stretching vibration<sup>21,31,34,35</sup> of the Si—O—Si group at

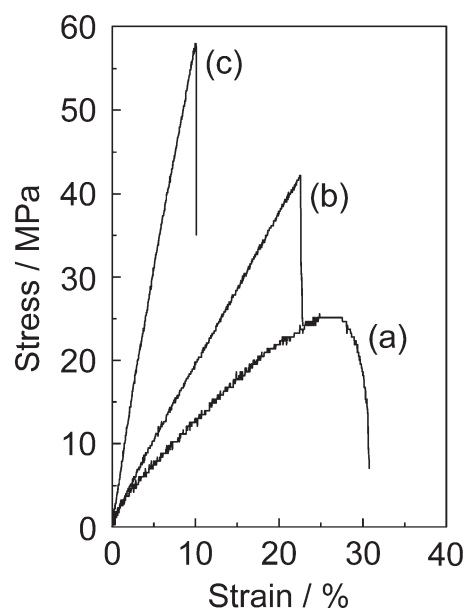


**Figure 3.** TG (a) and DTA (b) curves of pectin-SiNSi composite material at the heating rate of  $10^{\circ}\text{C min}^{-1}$  to  $300^{\circ}\text{C}$  under a dry-nitrogen flow. (1) pectin without the addition of an inorganic component (2) pectin-30 wt % SiNSi composite, (3) pectin-50 wt % SiNSi composite, (4) pectin-80 wt % SiNSi composite, and (5) dried SiNSi materials. Triplicate experiments gave similar results.

$1000\text{--}1200\text{ cm}^{-1}$  appeared. Generally, the trimethoxysilyl group, such as  $\text{—Si}(\text{OCH}_3)_3$  group in SiNSi, hydrolyzes stepwise in water to give the corresponding silanols, and ultimately condense to siloxanes.<sup>36</sup> Therefore, the formation mechanism of pectin-SiNSi composite material is proposed as follow: the methoxy group of the SiNSi molecules hydrolyzed and formed the network of the  $\text{Si—O—Si}$  group by polymerization in the composite material [see the condensation reaction of SiNSi in Figure 1(b)]. At the same time, the  $\text{—NH}_2^+$  group of the SiNSi forms the cross-linking structure with the  $\text{—COO}^-$  group of pectin by the electrostatic interaction. Additionally, the three-dimensional network structure of SiNSi encapsulates the pectin molecule in its network. Therefore, the pectin-SiNSi composite materials provided the water-insoluble property. Scheme 1(c) shows the structural model of pectin-SiNSi composite material with the cross-linking between SiNSi and pectin.

#### Thermal Stability of Pectin-SiNSi Composite Material

Figure 3(a,b), respectively, show the TG analysis and DTA curves of (1) pectin without the addition of the inorganic component (2) pectin-30 wt % SiNSi composite, (3) pectin-50 wt % SiNSi composite, (4) pectin-80 wt % SiNSi composite, and (5) dried SiNSi materials at the heating rate of  $10^{\circ}\text{C min}^{-1}$  up to  $300^{\circ}\text{C}$  under a dry-nitrogen flow. The TG weight loss of the pectin without the addition of SiNSi was approximately 50% at  $250^{\circ}\text{C}$ . In addition, the pectin molecule showed endothermic and exothermic peaks at  $45^{\circ}\text{C}$  and  $220^{\circ}\text{C}$ , respectively. The endothermic and exothermic peaks are due to the evaporation of water and the thermal decomposition of the pectin, respectively. The exothermic peak at  $220^{\circ}\text{C}$  increased with an increase in the addition of SiNSi and disappeared at  $\geq 50$  wt % SiNSi. These results suggested that the thermal stability of the pectin-containing material increased due to addition of the inorganic component, such as the SiNSi molecule. This is due to the formation of a three-dimensional (3D) network with the electro-



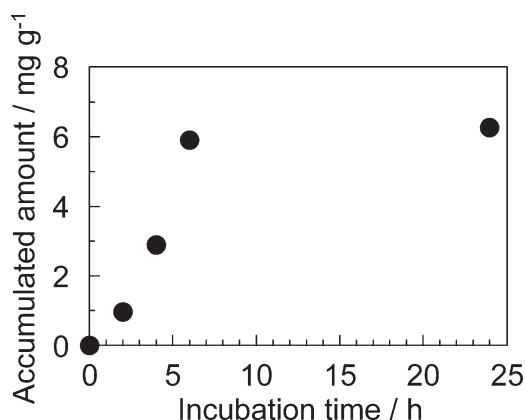
**Figure 4.** Stress-strain curves of (a) pectin without the addition of an inorganic component, (b) pectin-10 wt % SiNSi composite, and (c) pectin-30 wt % SiNSi composite materials, respectively. These measurements were done at  $25^{\circ}\text{C}$  under a  $50 \pm 5\%$  relative humidity conditions. The initial length of the membrane was 5 mm and the separation rate was  $10\text{ mm min}^{-1}$ . Pentaplicate experiments gave similar results.

static interaction between the pectin molecule and SiNSi molecule. Similar phenomena, such as the increase in the thermal stability due to addition of the inorganic component into the organic material, have been reported for various organic-inorganic composite materials.<sup>21,37–39</sup> In contrast, the TG weight loss and endothermic peak of the composite material at  $<100^{\circ}\text{C}$  are due to the evaporation of water from the material.

#### Mechanical Strength of Pectin-SiNSi Composite Material

We measured a physical property, such as the mechanical strength, of the pectin-SiNSi composite materials. Figure 4(a–c) show the stress-strain curves of pectin without the addition of the inorganic component, pectin-10 wt % SiNSi composite, and pectin-30 wt % SiNSi composite materials, respectively. When the stress was loaded on the pectin material, the pectin broke at 26 MPa. The elongation at the break point of the pectin was approximately 25%. Similar measurements demonstrated at the pectin-SiNSi composite material. The broken stress increased with the addition of the inorganic component. The maximum broken stress was 58 MPa for the pectin-30 wt % SiNSi composite material. This value was approximately twice as high as that of the pectin without the addition of SiNSi. This is due to the composite effect by the mixing of the pectin and inorganic component which provides the mechanical strength. A similar effect, such as the increase of mechanical strength by the addition of inorganic component, was obtained for the double-stranded DNA-SiNSi hybrid material.<sup>21</sup> In contrast, the elongation of the composite material decreased with the increasing of mixing ratio. These phenomena are due to the formation of a 3D network consisting of the inorganic component and the flexibility of the pectin is lost by the SiNSi addition.





**Figure 5.** Accumulation of Cu(II) ions by pectin-SiNSi composite material for various incubation times. The concentration of the Cu(II) ions was 10 ppm. Each of the values represents the mean of three separate determinations.

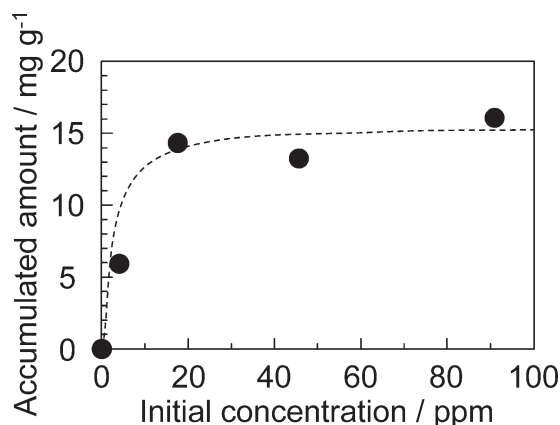
#### Accumulation of Metal Ion by the Pectin-SiNSi Composite Material

The water-insoluble pectin-SiNSi composite material contained the carboxy group, which can interact with various metal ions. Therefore, we demonstrated the accumulation of metal ions by the pectin-SiNSi composite material. When the pectin-SiNSi composite film was incubated in an aqueous Cu(II) ion-containing solution for 24 h, the composite film turned blue by the accumulation of the Cu(II) ions. Figure 1(b) is a photograph of the blue composite film stained with Cu(II) ions. In addition, the pectin-SiNSi composite material, which was stained by the Cu(II) ions, did not show any release of the Cu(II) ions in spite of its immersion in water. These results suggested that the pectin-SiNSi composite materials possessed an accumulative property of metal ions, such as the Cu(II) ions, in an aqueous solution. We next estimated the accumulative time of metal ions by the composite material. Figure 5 shows the accumulation of Cu(II) ions at various incubation times by the pectin-SiNSi composite material. The accumulated amount of Cu(II) ions increased with the incubation time and reached a constant value at 6 h. The accumulated amount was approximately 6  $\mu\text{g}$ . Therefore, we demonstrated the accumulation of metal ions for the incubation time of 6 h.

Figure 6 shows the accumulation of Cu(II) ions at various concentrations by the pectin-SiNSi composite material. The accumulated amount of Cu(II) ions increased with the initial concentration and reached a constant value at 20 ppm. The accumulated amount was 15  $\mu\text{g}$ . We defined the constant value as the maximum-accumulated amount of the metal ions. We calculated the molar ratio of pectin and accumulated metal ions at the maximum-accumulated amount. The molar ratio of pectin and metal ions was determined by eq. (2).

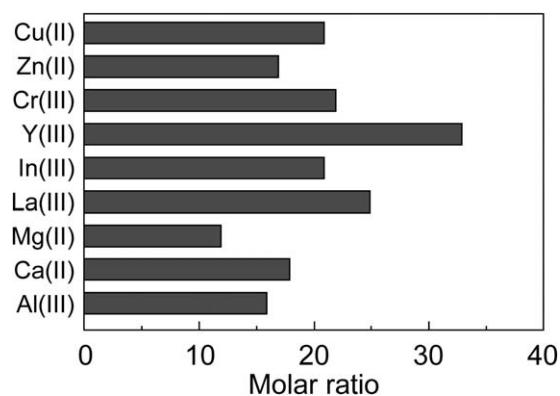
$$\text{Molar ratio} = \frac{[\text{Mole of pectin (sugar unit)}]}{[\text{Mole of accumulated metal ion}]} \quad (2)$$

where [Mole of pectin (sugar unit)] and [Mole of accumulated metal ion] were the moles of pectin (sugar unit) and the moles of metal ions at the maximum-accumulated amount, respectively. As a result, the molar ratio of pectin and Cu(II) ions was

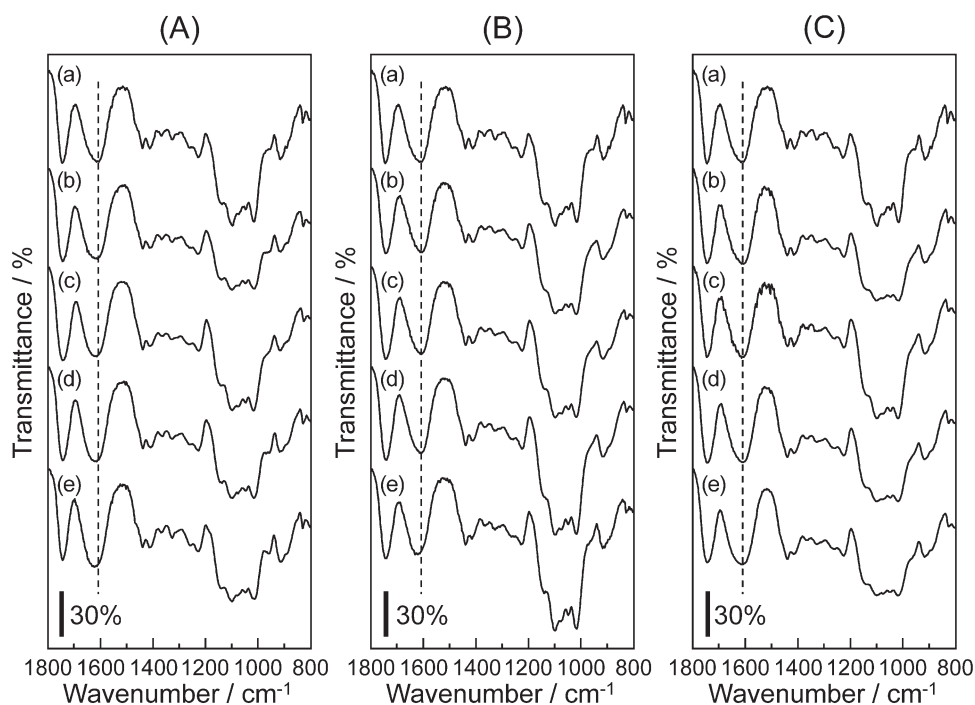


**Figure 6.** Accumulation of Cu(II) ion by pectin-SiNSi composite material for various concentrations. The incubation time was 6 h. Each of the values represents the mean of three separate determinations.

21. Therefore, we examined the accumulation of various metal ions by the pectin-SiNSi composite material, estimated the maximum-accumulated amount by a similar method, and then calculated the molar ratio by eq. (2). Figure 7 shows the molar ratio of pectin and metal ions for the maximum-accumulated amount. The molar ratios for the maximum-accumulated amount were different for the different kinds of metal ions. These values were 10–35. As the metal ions with the lower molar ratio strongly interact with the composite material, the binding affinities between the composite material and metal ions were  $\text{Mg(II)} \gg \text{Al(III)} > \text{Zn(II)} > \text{Ca(II)} > \text{Cu(II)}$ ,  $\text{In(III)} > \text{Cr(III)} > \text{La(III)} \gg \text{Y(III)}$ . These results suggested that the pectin-SiNSi composite material more strongly interacted with divalent metal ions than trivalent metal ions. Additionally, the orders of the ionic radii of the divalent and trivalent metal ions are  $\text{Mg(II)} < \text{Zn(II)} < \text{Cu(II)} < \text{Ca(II)}$  and  $\text{Al(III)} < \text{Cr(III)} < \text{In(III)} < \text{Y(III)} < \text{La(III)}$ , respectively.<sup>40,41</sup> Thus order of ionic radii is roughly consistent with the binding affinity between the composite material and metal ions. Generally, alginic acid, one of the acidic polysaccharides with a carboxy group, strongly interacts with the metal ions which possess a large ionic radius.<sup>42</sup> However, in our research, the



**Figure 7.** Molar ratios of pectin (sugar unit) and metal ions. The Moles of the accumulated metal ions were estimated from the maximum-accumulated amount. The molar ratios were calculated from eq. (2). Each of the values represents the mean of three separate determinations.



**Figure 8.** IR spectra of (A) Cu(II) ion-accumulated, (B) Mg(II) ion-accumulated, and (C) Y(III) ion-accumulated pectin-SiNSi composite materials. The concentrations of the metal ions were (a), 0 ppm; (b), 50 ppm; (c), 100 ppm; (d), 200 ppm; and (e), 500 ppm. The IR spectrum was measured at the resolution of  $4\text{ cm}^{-1}$ . Triplicate experiments gave similar results.

order of the binding affinity was opposite. Therefore, we obtained the IR measurements of the metal ion-accumulated pectin-SiNSi composite material to discuss the accumulative mechanism of the metal ions.

#### IR Measurements of Metal Ion-Accumulated Pectin-SiNSi Composite Material

Figure 8(A–C) show the IR spectra of the Cu(II) ion-accumulated, Mg(II) ion-accumulated, and Y(III) ion-accumulated pectin-SiNSi composite materials, respectively. Figure 8(a–e) shows the IR spectra of incubated samples at the concentrations of 0 ppm (composite material without the accumulation of a metal ion), 50 ppm, 100 ppm, 200 ppm, and 500 ppm, respectively. The composite material without the accumulation of metal ions had an absorption band at  $1604\text{ cm}^{-1}$  related to the symmetric stretching vibration of  $\text{—COO}^-$ .<sup>4,31–33</sup> For the Cu(II) ion-accumulated and Mg(II) ion-accumulated composite materials, this peak shifted to a higher wavenumber, ca  $15\text{ cm}^{-1}$ , with the increase in the concentration [see Figure 8(A,B)]. These results suggested that the metal ions interacted with the  $\text{—COO}^-$  group in the pectin molecule by an electrostatic interaction. In fact, the shift in the wavenumber by the interaction with metal ions has been reported for metal ion-accumulated polymers.<sup>4,24</sup> In contrast, the Y(III) ion-accumulated composite material, which indicated a low binding affinity to composite material (see Figure 7), almost did not show any shift in the absorption band at  $1604\text{ cm}^{-1}$  [see Figure 8(C)].

Generally, the pectin possesses a helical structure with a left-handed screw axis.<sup>2,43</sup> Additionally, the chelating between the carboxy groups of the pectin molecules with the divalent metal

ion stabilizes the helical structure of the pectin.<sup>1</sup> Similar phenomena occur in the pectin-SiNSi composite material. However, in the composite material, as the pectin molecules are included in the 3D network consisting of polymerized SiNSi and each chain has interacted by an electrostatic interaction, the helical structure in the pectin is distorted. As a result, the pectin in the composite material could not form the chelating structure and could not strongly interact with the metal ions of a larger ionic radius, such as the Y(III) ion.

#### CONCLUSION

We prepared a water-insoluble pectin-SiNSi composite material by mixing pectin and a silane coupling reagent, SiNSi. This organic-inorganic composite material possessed both the properties of flexibility of an organic material and the mechanical strength of an inorganic material. In addition, the pectin-SiNSi composite material could accumulate various metal ions. The binding affinities of the metal ions were  $\text{Mg(II)} \gg \text{Al(III)} > \text{Zn(II)} > \text{Ca(II)} > \text{Cu(II)}$ ,  $\text{In(III)} > \text{Cr(III)} > \text{La(III)} \gg \text{Y(III)}$ . The accumulative mechanism of the metal ions was related to the carboxy group of the pectin in the composite material. The pectin-SiNSi composite material may have potential use for environmental applications, such as the accumulation of various metal ions from drinking water, river water, industrial waste, and so forth.

#### ACKNOWLEDGMENTS

This work was supported by the Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science

and Technology of Japan (No. 25410195) and the matching fund subsidy for private universities from MEXT.

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