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Low Methoxylated Pectin for Preparation of an Intelligent Functional Sheet with Responsiveness to Sodium Ions

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ABSTRACT: A functional film is formed on a polyethylene nonwoven sheet by reaction of low methoxylated pectin with calcium chloride ($CaCl_2$) in the presence of ellagic acid. The film contains ellagic acid and functions as an intelligent material by releasing the ellagic acid in the presence of sodium ions. This response results from conversion of the water-insoluble pectin film to water-soluble pectin. The film with the best release of ellagic acid is produced using 0.5% $CaCl_2$ and 0.2% water-soluble pectin solutions. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: pectin film; intelligent material; Na^+ response; low methoxylated pectins

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INTRODUCTION

Intelligent materials can exhibit functionality in response to external stimuli such as temperature,[1–4] pH,[3–6] or chemicals.[7–9] Recent studies have investigated the application of intelligent materials as drug delivery systems,[3,4] self-repairing materials,[10,11] and intelligent windows.[12] In this study, we attempted to combine the concepts of intelligent materials and functional sheets. Functional papers are made with functional material(s) that are adsorbent, antimicrobial, or conductive.[13–15] Functional sheets utilize the native properties of the materials present in the sheet. By comparison, an intelligent functional sheet will give a functional response to external stimuli. We previously applied this concept to development of intelligent functional sheets that responded to humidity,[16] acid,[17] and sodium ion.[18] With humidity as an external stimulus,[16] the sheet produced color after a certain time and was able to, for instance, provide information about the moisture content of the air. In another study, we prepared a sheet that altered the odor it released from geraniol to acetic acid gas in response to acid.[17] The intelligent functional sheet, which could release moisturizer by responsive to sodium ion, was also prepared using sodium alginate.[18] In this study, the objective was to produce a sheet made with pectins as a natural polymer and make it functional in response to Na^+ (e.g., in sweat or urine) so that it could release a moisturizer (ellagic acid) to maintain the level of moisture in the skin.

Ellagic acid[19,20] is a polyphenolic compound found in fruit, such as strawberries, that has antibacterial and anti-inflammatory effects and can be used as a moisturizer. Pectin, which is present in plant cell walls, is used as a gelling agent in food products such as jams and bakery fillings.[21–24] The main components of pectins are α-(1-4)-linked D-galacturonic acid residues. The carboxyl group of the D-galacturonic acid is methyl esterified, and gel formation depends on the percentage of methyl esterified D-galacturonic acid, or degree of methoxylation.[22] Pectins can be classified as high methoxylated (HM, >50% methoxylated) or low methoxylated (LM, <50% methoxylated). In acidic conditions (pH<3.5), HM pectins precipitate because of decreased solubility and form a gel. The solubility decreases as carboxyl group dissociation is inhibited and the anionic charge decreases to neutralize the charge of the HM pectin. LM pectins contain many free carboxyl groups and form gels by a reaction between these carboxyl groups and multivalent ions such as calcium ions (Ca^{2+}).[22,23] Pectin gel formed by Ca^{2+} has a three-dimensional network ("egg box") structure,[22] and this can incorporate compounds such as ellagic acid. Theoretically, pectin gel could be used to fix ellagic acid on a substrate without a binder.[22] In earlier studies, functionalized sheets have been prepared by coating the functional materials with a binder to hold them on the surface of the sheet. However, a functional sheet prepared by this method would not be sufficiently functional for the purpose of this study, because the binder covering the surface of the functional material(s) would reduce the sheet's response.[18,25] Consequently, the lack of a binder is important because an intelligent material will not function properly if it is covered by a binder.

Additional Supporting Information may be found in the online version of this article.

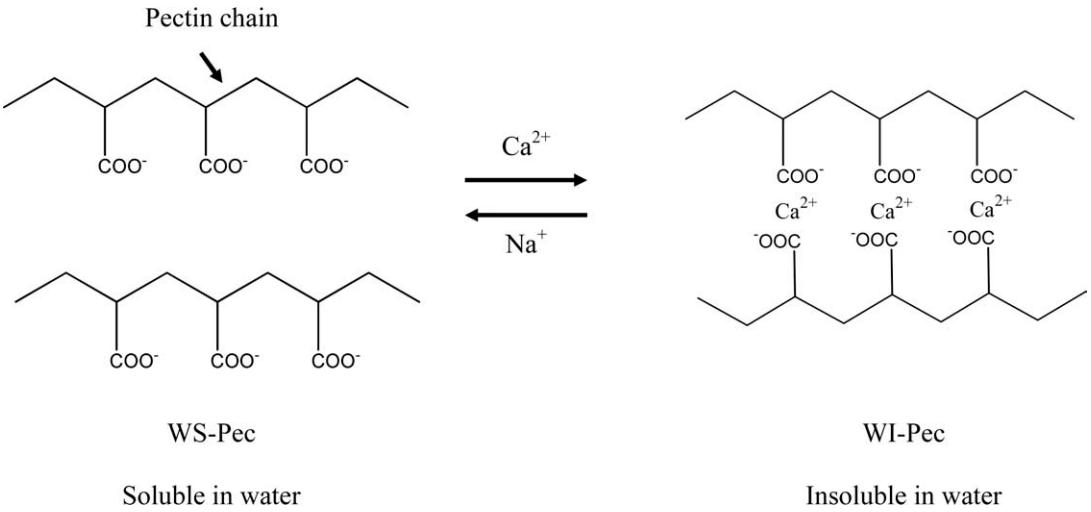

Figure 1. Ion exchange reaction between WS-Pec and WI-Pec.

In this study, calcium chloride ($CaCl_2$) was used to form a LM pectin gel containing ellagic acid directly on a polyethylene nonwoven sheet. The gel was converted to a film by drying to produce an intelligent material that was responsive to sodium ions (Na^+). In response to Na^+, the film released ellagic acid by a Na^+–Ca^{2+} ion exchange reaction, which converted the water-insoluble pectin (WI-Pec) film to water-soluble pectin (WS-Pec) (Figure 1). Thus, this method using pectins as the natural polymer is much simpler for preparation of intelligent material compared with the preparation method of other intelligent materials.[1–9] Additionally, the WI-Pec films before and after the Na^+ response were characterized using Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

WS-Pec (LM-104AS-J) was purchased from Sansho Co., (Osaka, Japan). Sodium chloride (NaCl) and $CaCl_2$ were purchased from Wako Pure Chemical Industries (Osaka, Japan). Nonwoven polyethylene for use as the substrate was supplied by Unicharm Corporation (Tokyo, Japan).

Preparation of WI-Pec Film Containing Ellagic Acid on the Polyethylene Surface

A 30 × 25 mm sheet of nonwoven polyethylene was impregnated with $CaCl_2$ by immersion in 50 mL of 0–1.0% (w/w) aqueous solution with stirring at 250 rpm. The impregnated film after the removal of excess $CaCl_2$ solution by filter paper was immersed in a 0.05–0.5% (w/w) WS-Pec solution (50 mL) containing ellagic acid (0.25 g) for 5 min, and then dried at 105°C for 30 min.

Evaluation of the Amount of Ellagic Acid Fixed on the Sheet by the Film

A 10 × 10 mm prepared sheet was immersed in 0.01 mol L^{-1} sodium hydroxide (5 mL) for 30 min at room temperature. After filtration of the solution using a membrane filter, a 1 μL aliquot was analyzed by high-performance liquid chromatography (HPLC) without further purification.

The ellagic acid concentration was determined using a HPLC (Separation Module 2695, Waters, Milford, MA) equipped with a C18 column (Gemini C18, 150 × 4.6 mm, I.D. 5 μm, Phenomenex, Torrance, CA) and a UV detector (254 nm). The mobile phase was acetonitrile : 20 mmol L^{-1} phosphorous acid solution (18 : 82 v/v), with constant flow rate of 1.0 mL min^{-1}. The column temperature was 40°C.

Evaluation of the Amount of Ellagic Acid Released from the Sheet in Response to Na^+

A 10 × 10 mm prepared sheet was immersed in 0.65% NaCl (3 mL) or distilled water (3 mL) for 30 min at room temperature in a laboratory dish. After the removal of the sheet and the residual WI-Pec film (not powder) containing ellagic acid which was larger than the free ellagic acid, the only fine powder of the free ellagic acid released from the WI-Pec film in the dish was then dried at 105°C. The ellagic acid residue was dissolved in 0.01 mol L^{-1} NaOH (3 mL). After filtration of the solution with

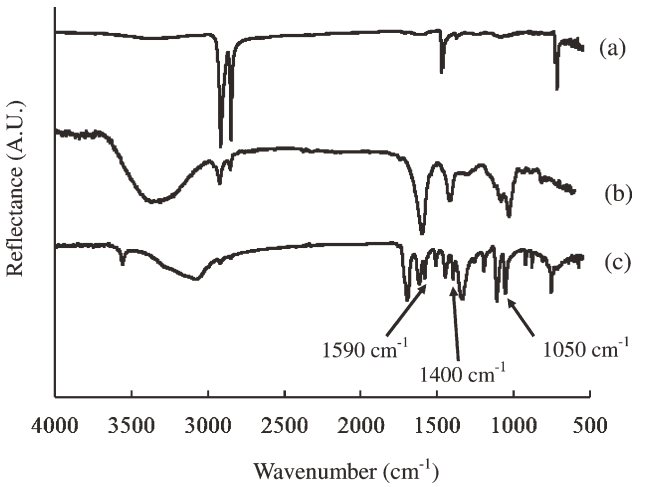

Figure 2. FT-IR spectra of (a) the blank polyethylene sheet, and (b) the polyethylene sheet coated with WI-Pec film without and (c) with ellagic acid. Film preparation conditions: 1.0% $CaCl_2$ solution, 0.5% WS-Pec solution, and 0 or 0.5% ellagic acid.

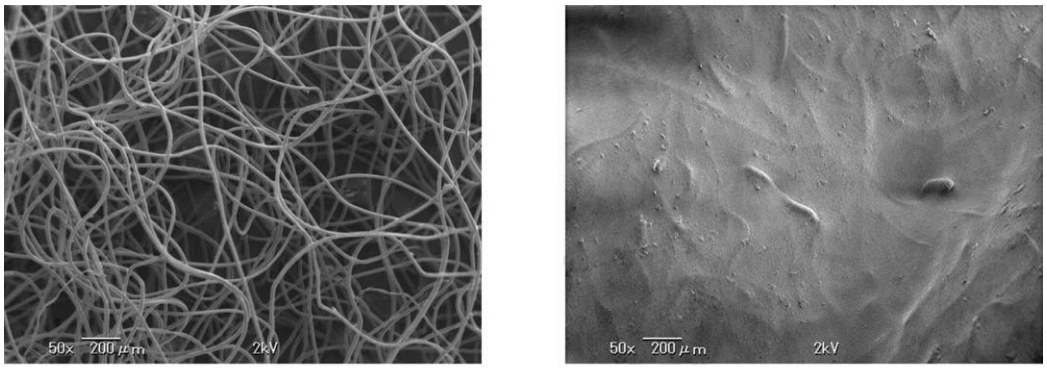

Figure 3. SEM images of (a) the blank polyethylene sheet and (b) the polyethylene sheet coated with WI-Pec film with ellagic acid. The film preparation conditions are the same as in Figure 2.

a membrane filter, a 1 μL aliquot was analyzed by HPLC without further purification. The HPLC analytical conditions were the same as those detailed above.

The percentage of ellagic acid released from the film on the sheet when immersed in NaCl solution (RA_{Na}) or distilled water (RA_W) was evaluated using the following equations:

$$RA_{Na}(\%) = W_{Na}(gm^{-2})/W_0(gm^{-2}) \times 100$$
$$RA_W(\%) = W_W(gm^{-2})/W_0(gm^{-2}) \times 100$$

where W_{Na} and W_W are the amounts of ellagic acid released from the films on the sheets immersed in NaCl solution and distilled water, respectively, for 30 min; and W_0 is the amount of ellagic acid fixed on the sheet by the film.

Characterization of the WI-Pec Film Containing Ellagic Acid

FT-IR attenuated total reflection spectra were obtained using an FT-IR-6100 (Jasco, Tokyo, Japan) spectrometer at a resolution of 4 cm^{-1}. Forty-five scans were accumulated in the spectral range 4000–550 cm^{-1}. The surfaces of the WI-Pec films before and after the Na^+ response were analyzed using SEM (VE9800; Keyence, Osaka, Japan) with accelerating voltage of 2.0 kV.

RESULTS AND DISCUSSION

Characteristics of the WI-Pec Film Containing Ellagic Acid

Figures 2 and 3 show FT-IR spectra and SEM images, respectively, of polyethylene sheets treated with different WS-Pec and $CaCl_2$ solutions. A WI-Pec film did not form on the polyethylene sheet with 0% or 0.25% $CaCl_2$ and 0.05–0.1% WS-Pec solutions. By contrast, with 0.5–1.0% $CaCl_2$ or 0.25% $CaCl_2$ and 0.2–0.5% WS-Pec solutions, a WI-Pec film did form on the polyethylene sheet. Characteristic bands were observed in the FT-IR spectrum of the WI-Pec film [Figure 2(b)] without ellagic acid, including the C=O stretching vibration at 1590 cm^{-1}, a $-CH_2(C=O)$ in-plane bending vibration at about 1400 cm^{-1}, and a C—O—C stretching vibration at ~1050 cm^{-1}. For the WI-Pec film with ellagic acid, most of the bands could be attributed to ellagic acid except for the WI-Pec film peaks at about 1590, 1400, and 1050 cm^{-1} [Figure 2(c)]. Formation of the WI-Pec film on the polyethylene surface was also confirmed by SEM [Figure 3(b)].

The WI-Pec film was immediately formed by the reaction between the Ca^{2+} fixed in the pores of polyethylene and WS-Pec. As a result, the Ca^{2+} diffused from the polyethylene nonwoven sheet interacted with the carboxyl group of the WS-Pec and the WI-Pec gel formed on the surface of the polyethylene sheet. The gel formation was controlled by the reaction time, which was 5 min in our study.

Consequently, while pores were observed on the surface of the polyethylene nonwoven sheet, these disappeared after WI-Pec film formation. Particles observed on the WI-Pec film surface were thought to be ellagic acid.

Ellagic Acid Release from the WI-Pec Film in Response to Sodium Ions

The WI-Pec film containing ellagic acid was not obtained when 0%, 0.25% $CaCl_2$ and 0.05% WS-Pec solution used for the preparation of WI-Pec film with ellagic acid. The W_0 ranged from 0.0225 to 1.54 g m^{-2} (Table S1). By contrast, WI-Pec film on the polyethylene sheet prepared under the conditions of 0.5–1.0% $CaCl_2$ solution and 0.1–0.5% WS-Pec solution could be formed. The W_0 ranged from 3.22 to 8.38 g m^{-2}. This shows ellagic acid was fixed on the polyethylene sheet by the WI-Pec film and

Table I. Effect of Film Preparation Conditions on the Amount of Ellagic Acid Fixed on the Sheet by the Film (W_0), the Amount of Ellagic Acid Released from the Film After Immersion of the Sheet in NaCl Solution (W_{Na}) or Distilled Water (W_W), and the Percentage of Ellagic Acid Released from the Film After Immersion of the Sheets in NaCl Solution (RA_{Na}) and/or Distilled Water (RA_W)

Concentration of $CaCl_2$; WS-Pec solution (%)	W_0 (g m^{-2})	W_{Na} (g m^{-2})	W_W (g m^{-2})	RA_{Na} (%)	RA_W (%)
0.5; 0.1	3.22	1.54	0.0405	47.8	1.26
0.5; 0.2	8.38	5.32	0.00902	63.5	0.108
0.5; 0.5	4.46	1.12	0.00609	25.1	0.137
1.0; 0.1	5.22	0.738	0.0862	14.1	1.65
1.0; 0.2	7.72	3.88	0.00679	50.3	0.0880
1.0; 0.5	5.85	0.0954	0.00559	1.63	0.0956

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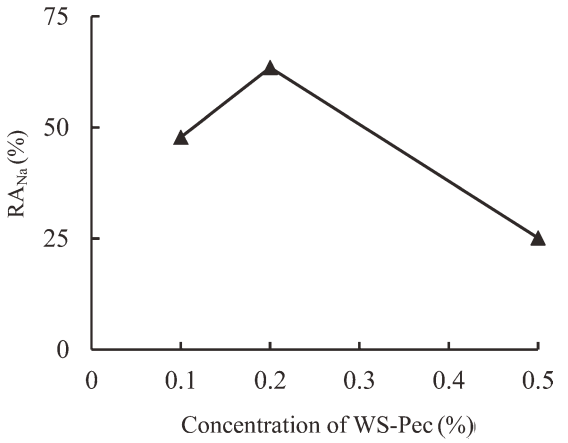

Figure 4. Effect of the film preparation conditions on RA_{Na}. Film preparation conditions: 0.1–0.5% WS-Pec solution, 0.5% ellagic acid, and 0.5% $CaCl_2$ solution.

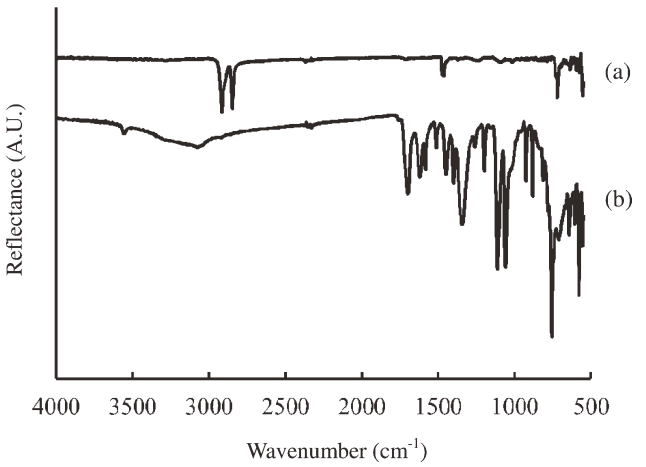

Figure 5. FT-IR spectra of films impregnated with (a) 0.65% NaCl solution and (b) distilled water. Film preparation conditions: 0.5% $CaCl_2$ solution, 0.2% WS-Pec solution, and 0.5% ellagic acid.

encapsulated in the film's three-dimensional network. In other words, the ellagic acid was fixed in "egg-box"[22] formed by the reaction between Ca^{2+} and carboxyl group in the WS-Pec solution and was mainly trapped by the physical interaction with the WI-Pec film. For WI-Pec films prepared using 0.5% $CaCl_2$ solution, 0.2% WS-Pec solution gave the highest amount of fixed ellagic acid among the WS-Pec solutions investigated in this study (Table I).

Solutions of 0.5% $CaCl_2$ and 0.1–0.5% WS-Pec were used in subsequent experiments because of their suitability for the fixation of ellagic acid.

As shown in Table I, RA_{Na} was larger than RA_W for almost all the films prepared in this study. Optimum ellagic acid release in response to Na^+ was observed for the film prepared with 0.5% $CaCl_2$ and 0.2% WS-Pec solutions (Figure 4). This WI-Pec film effectively trapped Na^+ and allowed efficient conversion of WI-Pec to WS-Pec for release of ellagic acid.

Figure 5 shows the FT-IR spectra of polyethylene sheets after impregnation with NaCl solution or distilled water. The bands attributed to WI-Pec and ellagic acid in Figure 2(c) were not present in the spectrum of the polyethylene sheets after impregnation with NaCl solution [Figure 5(a)]. SEM images [Figure 6(a)] also confirmed the absence of the WI-Pec film on the polyethylene sheet. For the sheet impregnated with distilled water, bands for WI-Pec and ellagic acid were observed [Figure 5(b)], and SEM images [Figure 6(b)] confirmed the presence of the WI-Pec film.

The sheets were prepared using 0.5% $AlCl_3$, $FeCl_2$, and $CuCl_2$ solution instead of 0.5% $CaCl_2$ solution in the same preparation method mentioned in experimental section and their functions of ellagic acid release were studied to investigate Na^+ selectivity of the WI-Pec sheet prepared using $CaCl_2$. The RA_{NA} of WI-Pec sheet prepared using 0.5% $AlCl_3$, $FeCl_2$, and $CuCl_2$ were 2.47, 4.60, and 0.00282%., respectively. These results suggested that the WI-Pec film prepared using Ca^{2+} released ellagic acid in response to $Na^{+,}$ and its functionality was selective to Na^+. Ellagic acid release is believed to result from an ion exchange reaction between Ca^{2+} in WI-Pec and Na^+ (Figure 1), which converts WI-Pec to WS-Pec. These results show that WI-Pec is soluble in the NaCl solution but not distilled water.

The RA_{Na} values of the WI-Pec films prepared using the 0.5% WS-Pec solution was much smaller than those of the films prepared using the 0.2% WS-Pec solution (Figure 4). Ellagic acid release from the 0.5% WS-Pec films was difficult because a large

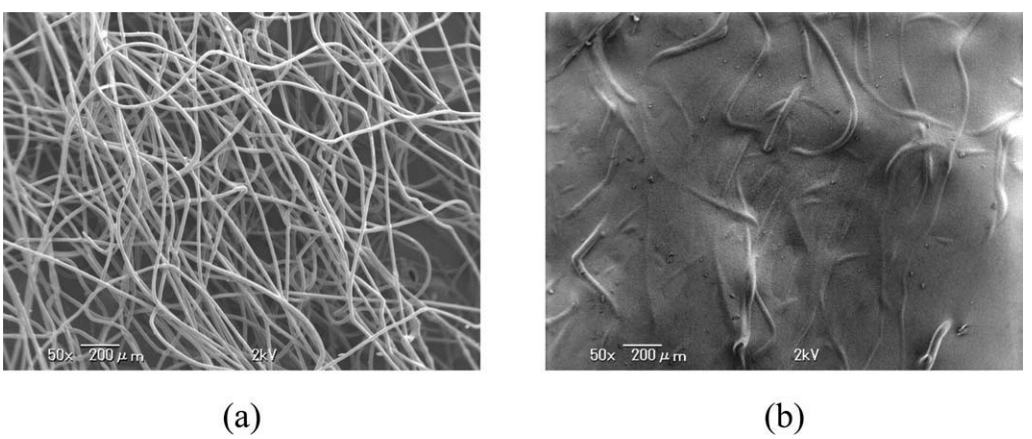

Figure 6. SEM images of films impregnated with (a) 0.65% NaCl solution and (b) distilled water. Film preparation conditions are the same as in Figure 5.

number of crosslinking sites (carboxyl groups) and cations resulted in many crosslinks in the film. In our previous study using sodium alginate as natural polymer,[18] the amounts of the ellagic acid by responsive to Na^+ decreased with increasing the sodium alginate solution. Therefore, the number of crosslinking sites increase with increasing the concentrations of the $CaCl_2$ and WS-Pec solutions and affect the ion exchange reaction.[18] Consequently, it was difficult for the ion exchange reaction between Ca^{2+} and Na^+ to occur, and the RA_{Na} values for WI-Pec films prepared using high concentrations of WS-Pec and $CaCl_2$ were very low.

The RA_{Na} values of the films formed using 0.05–0.1% WS-Pec solutions were smaller than those of the films formed using the 0.2% WS-Pec solution (Figure 4). These results can be attributed to the lower crosslink density of the WI-Pec films formed with 0.5% $CaCl_2$ solutions compared to the films formed with the 0.2% WS-Pec solution. In our previous study using sodium alginate as natural polymer,[18] the amounts of the ellagic acid by responsive to Na^+ decreased were smaller than other conditions when the sheet was prepared using low concentration of sodium alginate solution. The lower crosslink density would mean less Na^+ is retained in the ion exchange reaction because of less Ca^{2+} related to the ion exchange reaction. Additionally, as the less amount of ellagic acid entrapped in the gel, the release of ellagic acid would be lower.[18]

Therefore, the sheet prepared by the 0.5% $CaCl_2$ and 0.2% WS-Pec solutions had the most effective for the fixation of ellagic acid and the release of ellagic acid by responsive to Na^+.

These results show that adsorption of Na^+ and the ion exchange reaction between Ca^{2+} and Na^+ are important for release of ellagic acid from the film prepared using LM-pectins in response to Na^+. Ellagic acid release mainly depends on the concentrations of the WS-Pec and $CaCl_2$ solutions as the same as the results of the sheet prepared using sodium alginate.[18] LM-pectin is expected to be useful in the preparation of sheets for release of a variety of functional materials in response to Na^+.

CONCLUSIONS

A WI-Pec film containing ellagic acid was formed on the surface of a polyethylene nonwoven sheet by a reaction between the carboxyl groups of WS-Pec and Ca^{2+}. This film functioned as an intelligent material and released ellagic acid in response to Na^+. The WI-Pec film was converted to WS-Pec via ion exchange between Ca^{2+} and $Na^{+,}$ which resulted in release of ellagic acid. This function was dependent on the concentration of the $CaCl_2$ and WS-Pec solutions, and the 0.5% $CaCl_2$ and 0.2% WS-Pec solutions produced the film with the best ellagic acid release. This technique is expected to be useful in the preparation of sheets for release of a variety of functional materials in response to Na^+.

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