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Functional geraniol-$Ca(OH)_2$ composite/sodium acetate alginate film on nonwoven polyethylene sheet: acetic acid gas production in response to acid

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Abstract An alginate film, which released geraniol under ordinary conditions and produced acetic acid gas in response to acid, was directly prepared on a polyethylene nonwoven sheet. This alginate film was composed of geraniol-calcium hydroxide [$Ca(OH)_2$] composite, which was prepared by mixing geraniol and calcium oxide (CaO), and sodium alginate solution (Na-Alg) containing sodium acetic acid (CH_3COONa). Geraniol release from the alginate film could be monitored over time. Optimal conditions for the alginate film preparation were 0.75 or 1.0% Na-Alg solution containing 10% (w/v) CH_3COONa. Acetic acid ($\sim$3.58 ppm) could be generated from the sheet under these conditions by dropping 1.0 M hydrochloric acid (0.3 mL) onto it. We successfully prepared a functional sheet, which changed its released odor from geraniol to acetic acid gas in response to acid.

Introduction

Intelligent materials can sense changes in environmental conditions, processing the sensed information, and then responding with a change or action. They may exhibit changes in response to temperature [1–4], pH [3–6] or chemicals [7–10]. Drug delivery systems [3, 4], self-repairing materials [11, 12] and an intelligent window [13] have been actively studied as applications for intelligent materials. We have attempted to apply the concept of intelligent materials to a functional paper [10, 14–16] made with adsorbent, antimicrobial or conductive material [17–19].

In this research, a nonwoven polyethylene sheet was functionalized with an alginate film that could alter the odor it released from geraniol under ordinary conditions to acetic acid gas in response to acid. Such a sheet could act as a sensor to provide a signal, in this case acetic acid generation in response to acid. This intelligent alginate polymer film contained sodium alginate (Na–Alg) solution, geraniol and sodium acetic acid (CH_3COONa) and was prepared directly on the nonwoven polyethylene sheet.

Na–Alg is used in the food, pharmaceutical and biotechnology industries and can form calcium alginate (Ca–Alg) gel in the presence of calcium ion (Ca^{2+}) [10, 20–24] (Fig. 1). Ca–Alg gel has been widely used to encapsulate drugs and enzymes and in other applications [10, 22–24]. In this study, we attempted to form a Ca–Alg gel containing geraniol and CH_3COONa directly on the nonwoven polyethylene sheet surface by reaction with Ca^{2+}. The gel was then converted to a film by drying the coated sheet at 105 °C. However, hydrophilic Na–Alg solution lacks affinity for hydrophobic geraniol. This would mean that if Na–Alg solution was applied in the preparation of a functional paper containing geraniol, the geraniol could not fix on the sheet surface. Thus, this study aimed to solve the above problem for the preparation of functional paper containing geraniol using Na–Alg solution. In this report, a geraniol-calcium hydroxide [$Ca(OH)_2$] composite was prepared using calcium oxide (CaO) to reduce the geraniol to powder and improve its affinity for the Na–Alg solution. As CH_3COONa is known to react with hydrochloric or sulfuric acid to produce acetic acid gas, it was used in the film to produce the required response.

The characteristics of the alginate film containing geraniol-$Ca(OH)_2$ composite and CH_3COONa formed on the nonwoven polyethylene sheet are presented in this report. Optimal conditions for preparation of the sheet were found.

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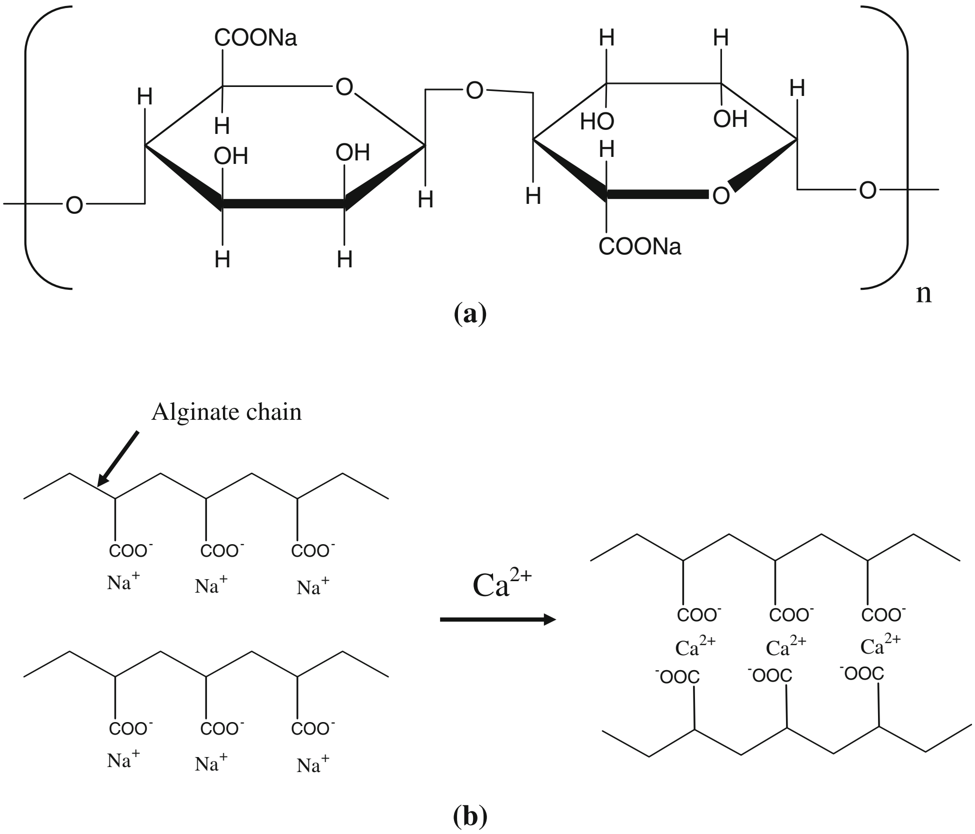


Fig. 1 **a** Structure of sodium alginate and **b** ion-exchange reaction between Na–Alg and Ca–Alg

Investigations were conducted on the effects of Na–Alg solution concentration and CH_3COONa concentration on the retention and release of geraniol from the sheet. In addition, the generation of acetic acid gas from the sheet in response to acid was studied and the concentrations of hydrochloric acid and CH_3COONa were investigated to elucidate the concentration of acetic acid gas generated from the sheet.

Experimental section

Materials

Sodium alginate (solution viscosity 80–120 mPa·s), trans-3,7-dimethyl-2,6-octadien-1-ol (geraniol, assay 90%), CaO, CH_3COONa, hydrochloric acid, ethanol and dichloromethane were purchased from Wako Pure Chemical Industries Ltd. Nonwoven polyethylene sheet used as the substrate was supplied by Unicharm Corporation. Acetonitrile and distilled water for high-performance liquid chromatography (HPLC) were purchased from Kanto Chemical Co., Inc.

Preparation of geraniol-$Ca(OH)_2$ composite

A mixture of CaO (8 g) and geraniol (4 g) was agitated using magnetic stirring for 5 min at 15 °C. During this time distilled water (10 mL) was added dropwise to the mixture. The geraniol-$Ca(OH)_2$ composite was dried at room temperature and then stored in the refrigerator at 4 °C.

Preparation of alginate polymer film containing geraniol-$Ca(OH)_2$ and CH_3COONa on the surface of nonwoven polyethylene sheet

The geraniol-$Ca(OH)_2$ composite (50 mg) was uniformly fixed on a 30 × 20 mm sheet of nonwoven polyethylene. This sheet was immersed in 0.1–1.0% (w/w) Na–Alg solution (50 mL) containing CH_3COONa (0–10 g) for 5 min, then dried at room temperature for 24 h.

Evaluation of geraniol fixation in the composite and its retention on the sheet

The geraniol-$Ca(OH)_2$ composite (0.1 g) and the sheet, prepared in the sections "Preparation of geraniol-$Ca(OH)_2$ composite" and "Preparation of alginate polymer film containing geraniol-$Ca(OH)_2$ and CH_3COONa on the surface of nonwoven polyethylene sheet", respectively, were immersed in 10 mL ethanol at room temperature for 10 min. After filtration of the solution using a membrane filter, a 1 µl aliquot was subjected to HPLC analysis without further purification. Geraniol concentration was determined using a HPLC (2695 Separation Module, Waters) equipped with a C18 column (Inertsil ODS-3, GL sciences Inc., 150 × 4.6 mm) and a UV detector (210 nm). The mobile phase was 70% acetonitrile/30% distilled water, with a constant flow rate of 1.0 mL min^{-1}. The column temperature was 40 °C.

The retention of geraniol fixed on the sheet was evaluated according to:

$$\text{Retention }(\%) = W_1/W_0 \times 100$$

where W_1 (mg) is the amount of geraniol fixed on the sheet and W_0 (mg) is the amount of geraniol in 50 mg of the geraniol-$Ca(OH)_2$ composite.

Evaluation of geraniol release from the sheet

The sheet was placed in a 50 mL vial and sealed with a silicon septum. Geraniol released from the sheet was collected using the silica-based absorptive $\mathrm{MonoTrap}^{\mathrm{TM}}$ (Rcc 18, GL sciences Co., Ltd.), which was inserted into the vial at 25 °C for 3–72 h. The geraniol trapped on the $\mathrm{MonoTrap}^{\mathrm{TM}}$ was extracted using dichloromethane (200 μL) and ultrasonic extraction for 5 min. The concentration of geraniol was analyzed by gas chromatography (GC, GC-2014, Shimadzu) equipped with a 30 m × 0.32 mm $\mathrm{SLB}^{\mathrm{TM}}$-5ms column (SUPELCO), a flame ionization detector, and using N_2 as the carrier gas.

The amount of geraniol released from the sheet (RA) was evaluated according to:

$$\mathrm{RA} = \mathrm{RA}_1/\mathrm{RA}_0$$

where RA_1 is amount of geraniol released from the sheet after 3–72 h and RA_0 is the initial amount of geraniol fixed on the sheet.

Evaluation of acetic acid gas generation from the sheet in response to acid

The sheet was placed in a 200 mL reaction vessel equipped with a glass cover and 0.1–1.0 M hydrochloric acid (0.3 mL) was dropped onto the sheet surface by microsyringe injection into the vessel. The concentration of acetic acid gas generated from the sheet in response to the injected acid was determined from 10 s to 30 min post-injection using a gas detector tube (81L, GASTEC Corporation).

Characterization of alginate film containing geraniol-$Ca(OH)_2$ composite and CH_3COONa on nonwoven polyethylene sheet

Fourier transform infrared (FT-IR) attenuated total reflection (ATR) spectra were obtained using an FT-IR-61000 (JASCO, Inc.) spectrometer at a resolution of 4 cm^{-1}. Forty scans were accumulated in the spectral range 4000–550 cm^{-1}. The sheet surface was analyzed using scanning electron microscopy (SEM, VE-9800, Keyence Corporation) with an accelerating voltage of 1.0–2.0 kV.

Results and discussion

Geraniol fixation in the geraniol-$Ca(OH)_2$ composite

The geraniol-$Ca(OH)_2$ composite was prepared (section "Preparation of geraniol-$Ca(OH)_2$ composite") to powderize the geraniol and improve its affinity to the Na–Alg solution. A photograph and SEM image were obtained of the geraniol-$Ca(OH)_2$ composite powder (Fig. 2). The amount of geraniol fixed in the geraniol-$Ca(OH)_2$ composite prepared in this study was 258 mg per 1 g $Ca(OH)_2$. The CaO was converted to $Ca(OH)_2$ by the exothermic hydration reaction with H_2O:

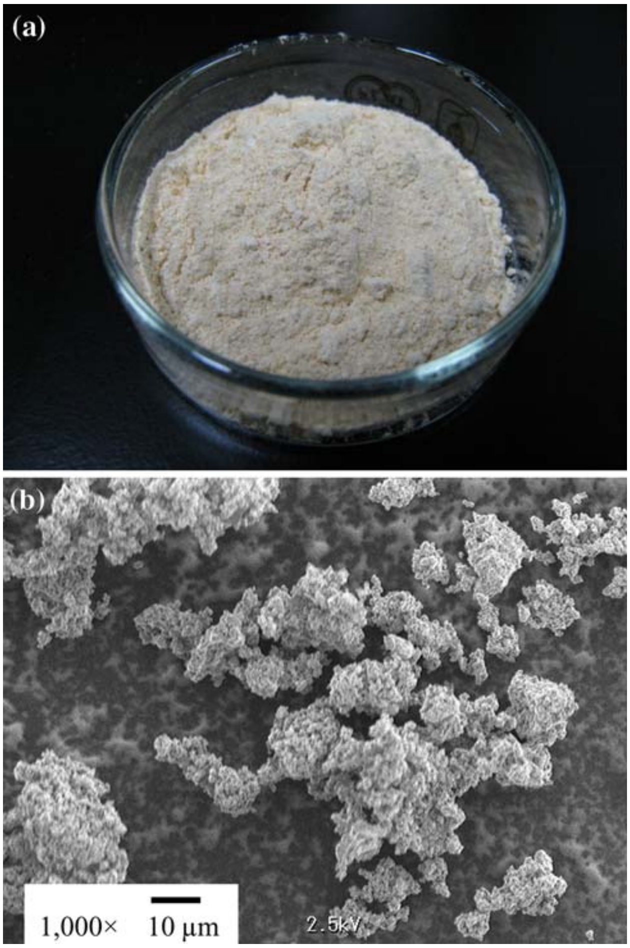


Fig. 2 Photograph (**a**) and SEM image (**b**) of the geraniol-$Ca(OH)_2$ composite powder

$CaO + H_2O \rightarrow Ca(OH)_2$ ($\Delta H = -63$ kJ/mol).

At that moment, the geraniol was thought to be adsorbed by $Ca(OH)_2$. This fixed the geraniol into a geraniol-$Ca(OH)_2$ composite and effectively powderized the geraniol.

Characteristics of the alginate film containing geraniol-$Ca(OH)_2$ composite and CH_3COONa formed on the sheet surface

The geraniol-$Ca(OH)_2$ composite was fixed to the fibers and pores of the nonwoven polyethylene sheet by physical bonding (Fig. 3b). However, as this bonding could not firmly retain the geraniol-$Ca(OH)_2$ composite on the sheet surface, the formation of the alginate film on the sheet was necessary for fixation.

Peaks attributed to the alginate film were observed in the FT-IR spectrum of the sheet prepared using Na–Alg solution containing the geraniol-$Ca(OH)_2$ composite and CH_3COONa (Fig. 4). These peaks included a C=O stretching vibration at 1550 cm^{-1}, a $-CH_2-$ in-plane bending vibration at about 1400 cm^{-1}, and a C–O–C stretching vibration at approximately 1020 cm^{-1} (Fig. 4b). SEM also confirmed formation of the alginate film on the nonwoven polyethylene surface (Fig. 3c). These results indicate that the alginate film on the sheet surface was formed by crosslinking between Ca^{2+} from the geraniol-$Ca(OH)_2$ composite (Fig. 3b) and the carboxyl group of the Na–Alg. This meant the alginate film containing the geraniol-composite and CH_3COONa could be formed on the sheet without the need of a binder. Turning the geraniol into a powder and forming the alginate film were effective for fixing the geraniol on the nonwoven polyethylene sheet.

Functional paper has typically been prepared by coating the functional materials with a binder. However, functional paper prepared in that manner might not be sufficiently functional for the purpose of this research because the surface of the functional alginate film would be covered with binder [25]. Consequently, a technique that fixes the alginate film directly on the sheet surface is important for the intelligent function. Therefore, the technique in this study was promising in that the functional paper was prepared without using a binder.

The retention and release of geraniol on the sheet

To calculate the retention of geraniol fixed on the sheet, W_0 was calculated to be 12.9 mg from the amount of geraniol-$Ca(OH)_2$ composite (50 mg) used in sheet preparation. The retention of geraniol fixed on the sheet was found to increase with increasing Na–Alg solution concentration (Fig. 5a). This increase in retention was in accord with the increase in viscosity of the Na–Alg solution. The viscosities of 0, 0.1, 0.5, 0.75, and 1.0% Na–Alg solutions were 15.2, 24.4, 55.6, 71.3, and 96.8 mP s, respectively. With a 0.1% Na/Alg solution, it was difficult to fix the geraniol-$Ca(OH)_2$ composite to the sheet because the low

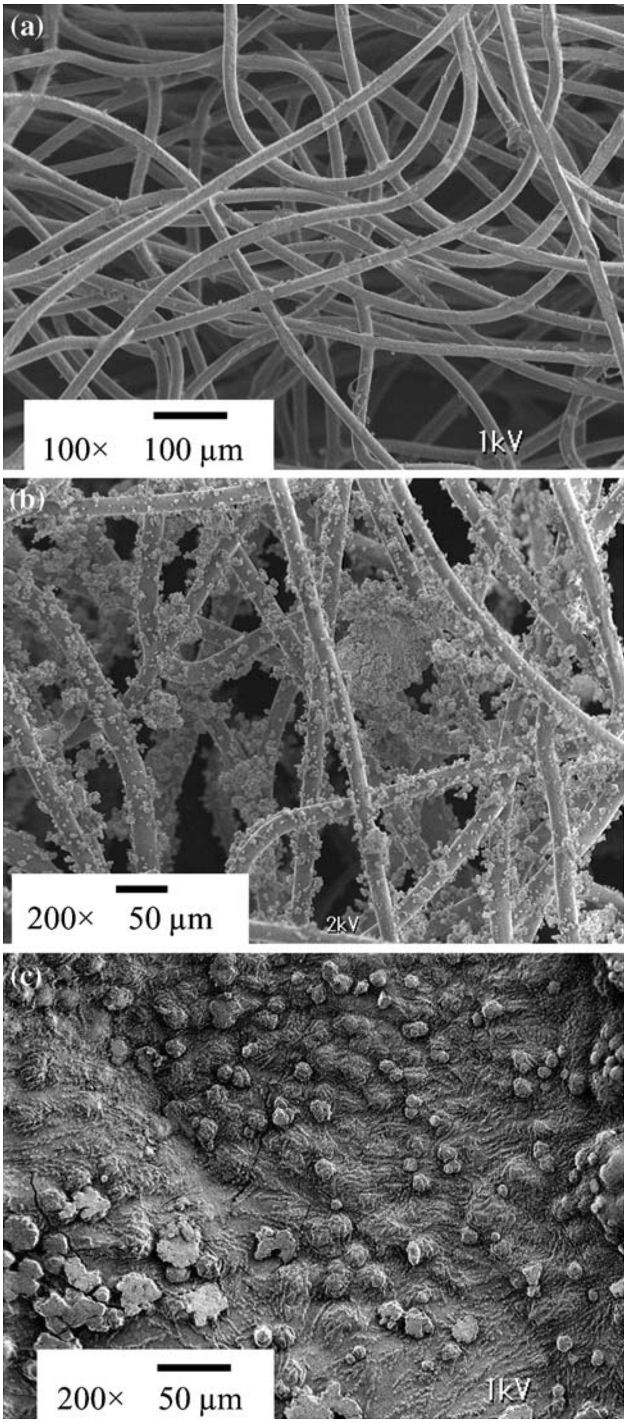


Fig. 3 SEM images of **a** blank sheet, **b** the geraniol-$Ca(OH)_2$ composite fixed on the nonwoven polyethylene sheet, and **c** sheet coated with alginate film containing the geraniol-$Ca(OH)_2$ composite and CH_3COONa. Experimental conditions for the alginate film application: 1.0% Na–Alg solution and 10% (w/v) CH_3COONa

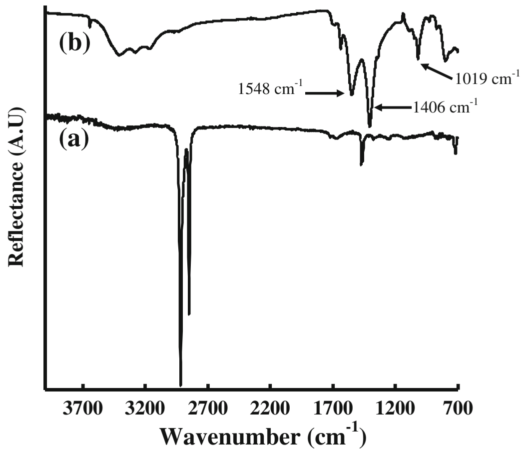


Fig. 4 FT-IR spectra of *a* blank sheet and *b* sheet coated with alginate film containing the geraniol-$Ca(OH)_2$ composite and CH_3COONa. Experimental conditions for the alginate film application: 1.0% Na–Alg solution and 10% (w/v) CH_3COONa

viscosity of the Na–Alg solution made the geraniol-$Ca(OH)_2$ composite separate from the sheet. These results indicated that the Na–Alg solution concentration was an important factor for the retention of geraniol-$Ca(OH)_2$ composite on the sheet.

The retention of geraniol fixed on the sheet also tended to increase as the concentration of CH_3COONa in the Na–Alg solution increased (Fig. 5b). The viscosities of a 1.0% Na–Alg solution containing 0, 10, and 20% (w/v) CH_3COONa were 96.8, 106.7, and 111.3 mP s, respectively. Similarly, the viscosities of a 0.75% Na–Alg solution containing 0, 10, and 20% (w/v) CH_3COONa were 71.3, 84.8, and 86.4 mP s, respectively. Therefore, the viscosity of the Na–Alg solution also tended to increase as the CH_3COONa concentration increased. However, when the concentration of CH_3COONa in the Na–Alg solution was 20% (w/v), the retention of the geraniol fixed on the sheet decreased. Fixation of the geraniol-$Ca(OH)_2$ composite on the sheet surface by crosslinking between Na–Alg and Ca^{2+} was thought to be hindered by excess CH_3COONa at this concentration.

These results indicated that the concentrations of both the Na–Alg solution and the CH_3COONa in it were important factors for retention of the geraniol-$Ca(OH)_2$ composite.

Figure 6 shows the amounts of geraniol released from the geraniol-$Ca(OH)_2$ composite and from the sheet prepared in the section "Preparation of alginate polymer film containing geraniol-$Ca(OH)_2$ and CH_3COONa on the surface of nonwoven polyethylene sheet". For the alginate film containing the geraniol-$Ca(OH)_2$ composite and CH_3COONa on the sheet, geraniol release was observed and the RA reached about 22% after 72 h. The RA of the geraniol-$Ca(OH)_2$ composite alone was about 30% after 72 h. These values were lower than the RA after 72 h for a blank sheet, which was prepared by dropping 10 mg of

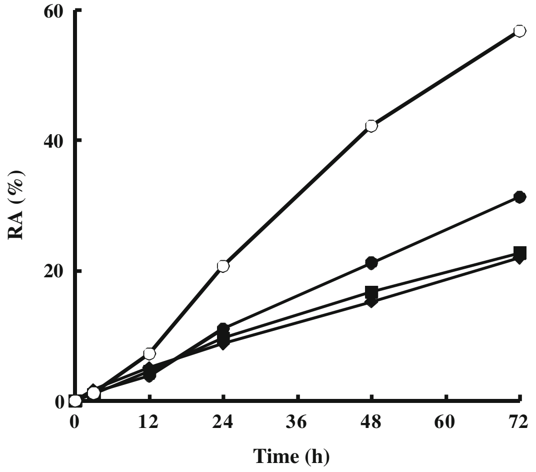
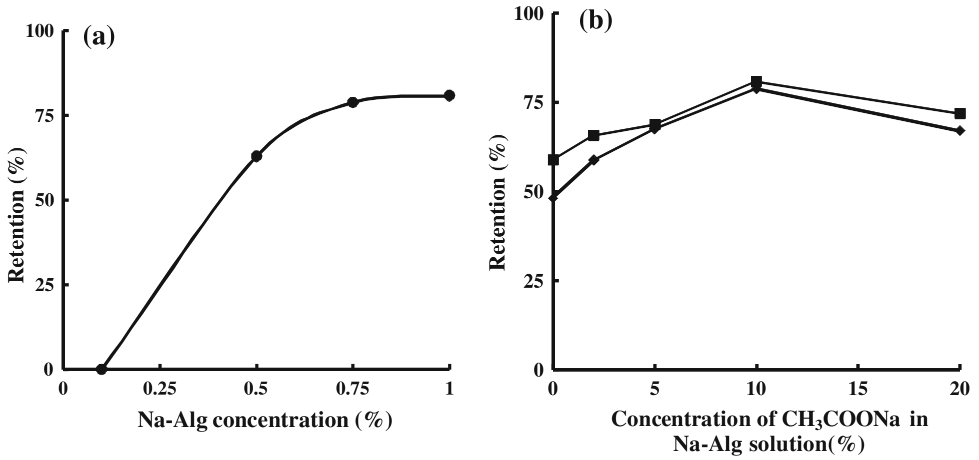


Fig. 6 Amount of geraniol released from (*circle*) blank sheet and (*filled circle*) geraniol-$Ca(OH)_2$ composite and alginate film prepared on the sheet. Experimental conditions for the alginate film application: (*filled square*) 1.0% or (*filled diamond*) 0.75% Na–Alg solution and 10% (w/v) CH_3COONa

Fig. 5 Retention of geraniol fixed on the sheet. Experimental conditions for the alginate film application: **a** 0–1.0% Na–Alg solution and 10% (w/v) CH_3COONa; **b** (*filled square*) 1.0% or (*filled diamond*) 0.75% Na–Alg solution and 0–20% (w/v) CH_3COONa



geraniol onto the nonwoven polyethylene sheet. These results indicate that both geraniol-Ca$(OH)_2$ composite alone and in an alginate film fixed on the nonwoven polyethylene sheet have a higher function for sustained release of geraniol compared with the blank sheet. Thus, the preparation of geraniol-Ca$(OH)_2$ composite powder and the preparation of the alginate film on the sheet surface were important for the sustained release of geraniol from the sheet. Optimal conditions for the alginate film prepared on the sheet were 0.75% or 1.0% Na–Alg solution containing 10% (w/v) CH_3COONa.

Generation of acetic acid gas from the sheet in response to acid

Figure 7 illustrates the concentration change in acetic acid gas generated by the sheet in response to acid. The sheet generated acetic acid gas as soon as it was exposed to acid. After 5 min, the concentration of acetic acid gas generated reached 3.58 ppm. This concentration was the maximum generated in this study, and it was still at this level after 30 min. Acetic acid gas was generated by the reaction between CH_3COONa and acid as follows:

$$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl.$$

The reaction between 100 mg of CH_3COONa and 0.3 mL of 1.0 M hydrochloric acid generated 33.8 ppm of acetic acid gas. Therefore, the amount of CH_3COONa in the alginate film prepared on the sheet was about 0.018 mg/mm^2.

The concentration of acetic acid gas generated from the sheet in response to acid after 3 min was used to evaluate the effect of changing the CH_3COONa concentration in the Na–Alg solution (Fig. 8a) and the hydrochloric acid concentration (Fig. 8b). When 0% CH_3COONa and 0.1 M hydrochloric acid were used, the sheet could not produce acetic acid gas in response to acid. The concentration of acetic acid gas generated from the sheet in response to acid increased with increasing CH_3COONa and hydrochloric acid concentrations.

These results showed that the sheet prepared in this study could alter the odor it released from geraniol to acetic acid gas in response to acid.

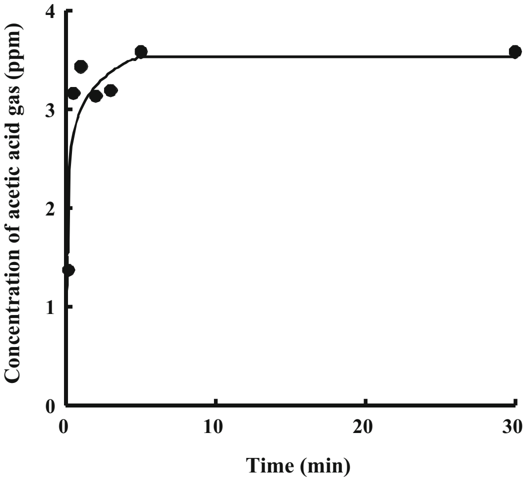
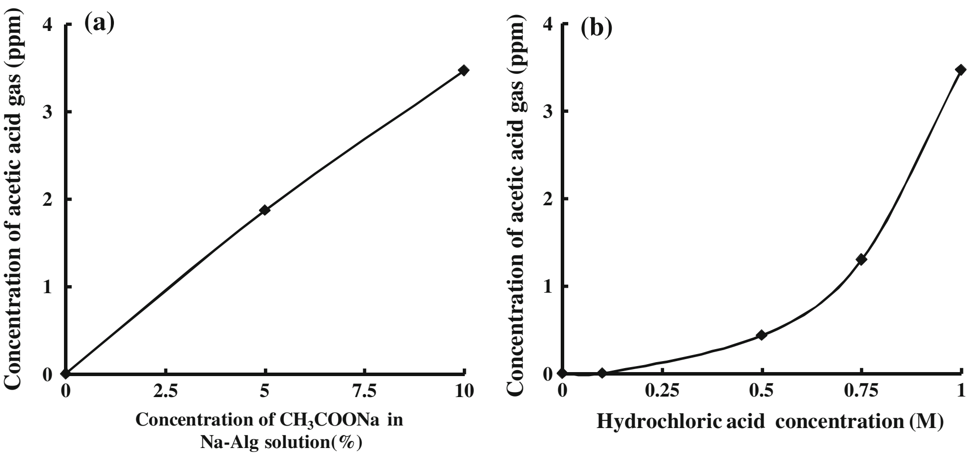


Fig. 7 Changes in the concentration of acetic acid gas generated from the alginate film prepared on the sheet in response to 1.0 M hydrochloric acid. Experimental conditions for the alginate film application: 0.75% Na–Alg solution and 10% (w/v) CH_3COONa

Conclusions

The geraniol-Ca$(OH)_2$ composite could be prepared using the hydration reaction of CaO to powderize the geraniol and improve its affinity to the Na–Alg solution. The alginate film containing the geraniol-Ca$(OH)_2$ composite and CH_3COONa could be formed directly on the sheet surface by reaction between Ca^{2+} from composite and the carboxyl group of the Na–Alg solution. Powderizing the geraniol and preparing the alginate film directly on the sheet surface without using a binder produced a film that performed

Fig. 8 Concentration of acetic acid gas generated from the alginate film prepared on the sheet in response to **a** 1.0 M hydrochloric acid and **b** 0–1.0 M hydrochloric acid after 3 min. Experimental conditions for the alginate film application: **a** 0.75% Na–Alg solution and 0–10% (w/v) CH_3COONa; **b** 0.75% Na–Alg solution and 10% (w/v) CH_3COONa



sustained release of geraniol. The geraniol retention and the amount of geraniol released from the sheet reached maximum values when the preparation conditions were 0.75 or 1.0% Na–Alg solution containing CH_3COONa of 10% (w/v). Acetic acid gas could be generated from the alginate film in response to acid and its maximum concentration was about 3.58 ppm. This technique is expected to be useful in the preparation of intelligent functional sheets that can alter the odor they release from geraniol to acetic acid gas in response to acid.

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