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Preparation of microcapsules that produce color in response to humidity for use in intelligent functional paper

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In this study, a microcapsule that produces color in response to moisture in air was produced for use in an intelligent functional paper which is able to self-color after a fixed time. This microcapsule containing $FeSO_4$ as the coloring material was prepared from gelatin and terephthaloyl chloride by an interfacial polymerization technique and was modified by a 2-propanol solution of glycerin to supplement the moisture sensitivity. A microcapsule membrane was formed by crosslinking between the amino group at the end of the gelatin and the carbonyl group of the terephthaloyl chloride. The time required for the microcapsules to produce the color tended to increase with decreasing amounts of the glycerin 2-propanol solution used for the soaking treatment of the microcapsules or increasing amounts of $FeSO_4$ in the microcapsules.

1. Introduction

Intelligent materials are defined as materials that have three main functions: sensing changes in environmental conditions, processing the sensed information and finally making a judgment [1–20]. These materials exhibit changes in response to external stimuli such as pH [1–4], temperature [2, 5–11], chemicals [12–14], electric fields [15] and light [16, 17]. Such intelligent materials have been required for drug delivery systems [5–9, 12–14] and self–repairing materials [18], and an intelligent window [16] has been actively studied. In this study, it was attempted to apply the concept of intelligent material to a functional paper.

Functional paper is paper made with functional material such as adsorbent, antimicrobial material or conductive material [19–21]. Functional paper utilizes the native properties of the materials present in the paper. On the other hand, intelligent functional paper demonstrates a function in response to external stimuli. In this study, intelligent functional paper was prepared using microcapsules applied to thermal paper and pressure-sensitive paper. Microcapsules are useful [1, 9–11, 18, 22–27] for protecting functional materials inside them from environmental factors for a long time, and for controlling the release of desired materials and the conversion of a liquid to the solid state. Additionally, microcapsules with various pH and temperature responses have been investigated and these performed their function by stimuli-response [1, 9–11, 18]. Intelligent functional papers prepared using microcapsules containing a thermo chromic and a photo chromic have been reported [28]. These papers exhibited changes of color in response to temperature or light. Therefore, microcapsules are thought to be useful for preparing intelligent functional paper.

In this work, the preparation of microcapsules that produce color after a fixed time, in response to moisture in air, was attempted. This was done in order to produce intelligent functional paper that is able to, for instance, provide information about the term of validity of a contract. The characteristics of color-producing microcapsules prepared are presented in this report. In addition, the effects of the amounts of glycerin and iron (II) sulfate heptahydrate ($FeSO_4$) (as a coloring agent) in the microcapsules on the time required for the color production of the microcapsules (color-producing time) were investigated to allow control of the color-producing time of the microcapsules.

2. Experimental section

2.1. Preparation of microcapsules

An aqueous solution of 25% (w/v) gelatin (1.5 ml) and 0.5–2% (w/v) iron (II) sulfate heptahydrate ($FeSO_4$) (1 ml) was poured into a cyclohexane solution (10 ml) containing sorbitan trioleate (SPAN 85) (0.6 g) as an

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emulsifier and the mixture was agitated at 500 rpm using magnetic stirring for 10 min at a room temperature. Subsequently, a cyclohexane solution (10 ml) of terephthaloyl chloride (TC) (0.1 g) was added to the mixture. This mixture was stirred (500 rpm) for 20 min at room temperature. The reaction mixture was then left in a refrigerator at 4°C for 12 h. The microcapsules isolated by filtration were washed with cyclohexane and deionized water in that order and were dehydrated by 2-propanol. Next, these microcapsules were impregnated with a 50 or 70% 2-propanol solution of glycerin. Gelatin, $FeSO_4$, SPAN 85, TC and glycerin were purchased from Wako Pure Chemical Industries, Ltd., Japan, and cyclohexane and 2-propanol were obtained from Kanto Kagaku, Japan.

2.2. Characterization of microcapsules

The shapes and the sizes of the microcapsules were investigated by a stereomicroscope (SZX-12, Olympus Co.) and a profile projector (V-12, NIKON Co.). Fourier transform infrared (FT-IR) spectra were measured on a FT-IR-480 (JASCO, Inc.) using attenuated total reflection (ATR) at a resolution of 4 cm^{-1} throughout the spectral range (4000–700 cm^{-1}), and accumulation of 100 scans. The elemental composition of the microcapsules was analyzed by scanning electron microscopy (SEM, JSM-5510LV, JEOL Inc.) and energy dispersive X-ray spectroscopy (EDS, Genesis 2000, EDAX Inc.) with an accelerating voltage of 20 kV after the microcapsules were coating with Au.

2.3. Color-producing study

Microcapsules obtained as described in Section 2.1 were placed on filter paper (Toyo Roshi Kaisha, Ltd.) soaked in a 0.5% aqueous solution of tannic acid and a 0, 50 or 70% 2-propanol solution of glycerin. Experimental conditions are presented in Table I. The times required for the development of the violet color of microcapsules settled on the filtration paper were determined with a stopwatch. The time measured as mentioned above was defined as the "color-producing time". The relative humidity and temperature were about 50% and 23°C, respectively.

TABLE I Glycerin concentration (2-propanol solution) used in microcapsules and the filter paper for the color production

	Microcapsule membrane (%)	Filter paper (%)
A	70	70
B	50	70
C	70	50
D	50	50
E	70	0
F	50	0

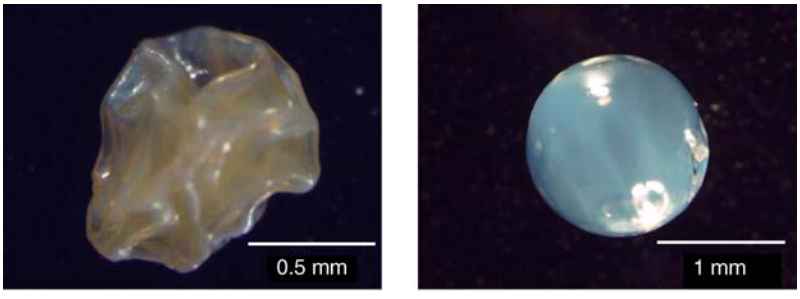
3. Results and discussion

3.1. Characteristics of the microcapsules

The yield, particle size and membrane thickness of the microcapsules prepared in this study were about 70%, 980 μm and 8.0 μm, respectively.

Fig. 1a shows the stereomicroscope image of a microcapsule prepared without adding TC to the reaction mixture. This microcapsule exhibited a reddish brown color, which is a characteristic color of Fe_2O_3. This result was thought to be caused by the crosslinking between the carboxyl group at the end of the gelatin and Fe^{2+}. Therefore, the membrane of this microcapsule could not be formed.

In contrast, a microcapsule prepared with TC and 0.5% $FeSO_4$ showed a white color as shown in Fig. 1b and could form a microcapsule membrane. Fig. 2a and b show the FT-IR spectra of the gelatin and the resultant microcapsule, respectively. It is well known that gelatin is composed of polypeptide chains consisting of different amino acids (Fig. 3a) arranged in a unique sequence. Accordingly, three characteristic peaks due to a C═O stretching vibration at around 1640 cm^{-1}, an N─H bending vibration at around 1550 cm^{-1} and a C─N stretching vibration at around 1230 cm^{-1}, attributed to a C─N─H bond, were observed, as shown in Fig. 2. An N─H peak was shown as a broad adsorption at 3700–3100 cm^{-1}. In Fig. 2b, new peaks at around 1790 cm^{-1} and 1723 cm^{-1} appeared, and these were attributed to an acid halide group and a carbonyl group of the TC (Fig. 3b), respectively. Additionally, the new peaks at around 1680 and 1282 cm^{-1} shown in Fig. 2b were supposed to be caused by a C═O peak and a C─N peak, respectively, from the aromatic amide formed by the reaction between the amino group at the end of the gelatin chain and the carbonyl group of TC.



(a) (b)

Figure 1 Stereomicroscope photographs of microcapsules prepared (a) without terephthaloyl chloride and (b) with terephthaloyl chloride in the reaction mixture, microcapsule preparation conditions: 25% gelatin, 0.5% $FeSO_4$ and 0–1% TC.

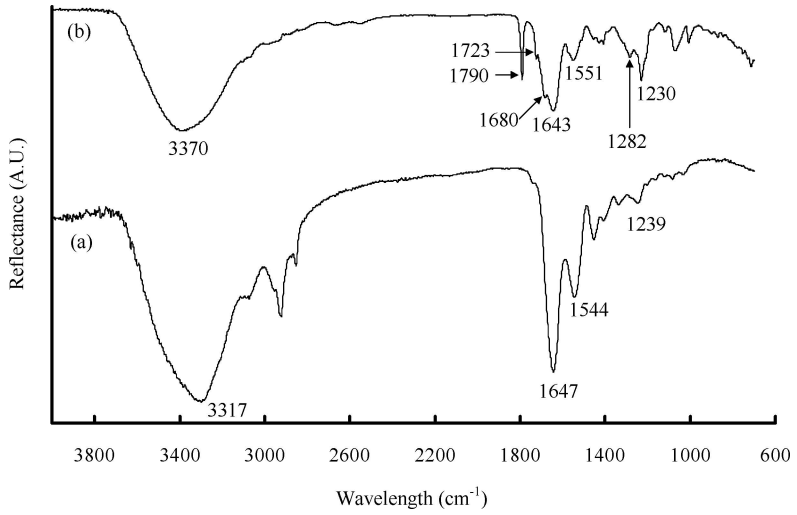


Figure 2 FT-IR spectra of (a) gelatin and (b) microcapsule, microcapsule preparation conditions: 25% gelatin, 0.5% $FeSO_4$ and 1% TC.

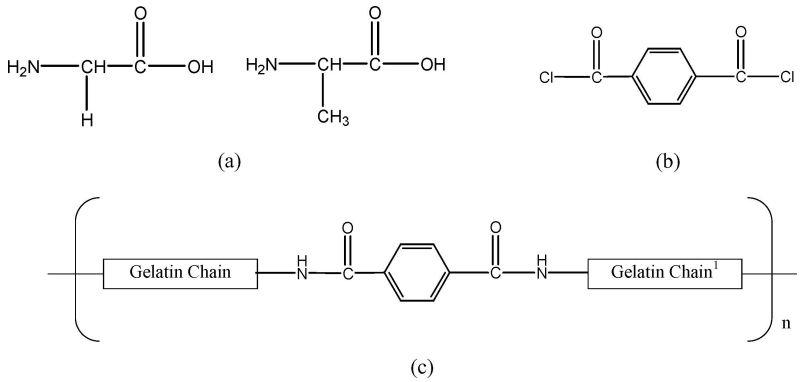


Figure 3 Chemical structures of (a) amino acids (glycine and alanine), (b) terephthaloyl chloride, (c) proposed crosslink between gelatin and TC.

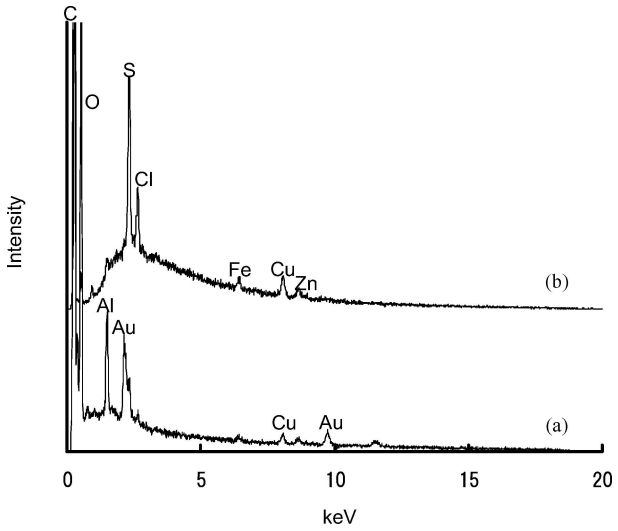


Figure 4 EDS spectra of (a) outside and (b) inside a microcapsule, microcapsule preparation conditions: 25% gelatin, 0.5% $FeSO_4$ and 1% TC.

The results shown in both Figs 1 and 2 indicate that the microcapsule membrane was formed by the crosslinking between gelatin and TC as shown in Fig. 3c.

Fig. 4 shows EDS spectra of the outside (a) and inside (b) of a microcapsule. Al, Cu and Zn, and Au found in the EDS spectra were attributed to the sample stand and the material used for coating the microcapsules, respectively. The main elements observed on the outside of the microcapsules were C and O. Inside the microcapsules, Fe and S peaks from $FeSO_4$ and Cl peaks from TC were obtained. These results suggest that $FeSO_4$ was present inside the microcapsule prepared by the interfacial polymerization reaction between gelatin and TC.

3.2. Color-producing study

Images of a microcapsule after the color production are presented in Fig. 5b.

Fig. 6 shows the effect of the amount of glycerin used in the modification on the color-producing time of the microcapsules containing 0.5% $FeSO_4$. Under conditions A and B (microcapsules placed on filtration paper treated with 70% glycerin solution), the color-producing times were about 4.0 and 5.5 h, respectively. The color-producing times for conditions C and D (microcapsules placed on filtration paper soaked in a 50% 2-propanol solution of glycerin) were 6.0 and 11.0 h, respectively. The color-producing times of conditions E and F were about 23.0 and 46.5 h, respectively. A microcapsule soaked with a less than 40% 2-propanol solution of glycerin could not carry out the color production. The coloring mechanism suggested is that the moisture adsorbed by the glycerin on the microcapsule membrane gradually disintegrates the microcapsule membrane and the reaction of $FeSO_4$

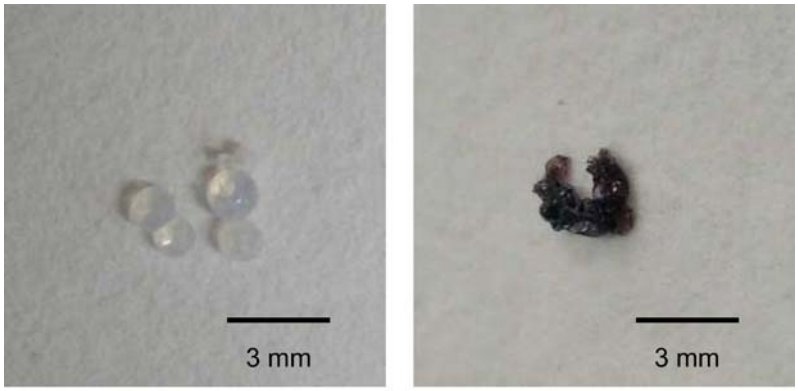


Figure 5 Photograph of a microcapsule (a) before and (b) after color production.

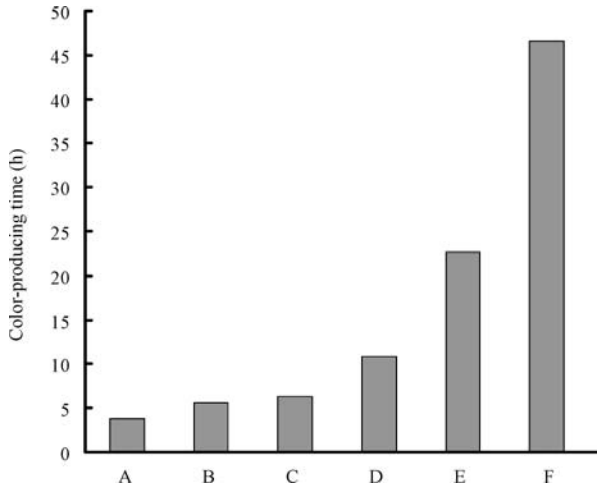


Figure 6 Effect of the amount of glycerin used in microcapsule modification on the color-producing time, microcapsule preparation conditions: 25% gelatin, 0.5% $FeSO_4$ and 1% TC.

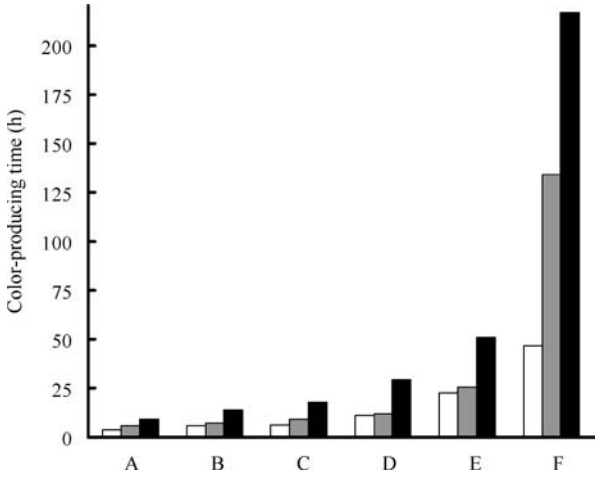


Figure 7 Effect of the amount of $FeSO_4$ in microcapsules on the color-producing time, microcapsule preparation conditions: 25% gelatin, 0.5-2% $FeSO_4$ and 1% TC, microcapsule soaked in 50% 2-propanol solution of glycerin. (□), 0.5% $FeSO_4$; (▒), 1% FeSO4; (■), 2% $FeSO_4$.

eluted from microcapsules with the tannic acid on the filtration paper results in a violet coloration. Accordingly, the moisture sensitivity of microcapsules soaked in less than 40% glycerin 2-propanol solution was not sufficient to ensure that the moisture captured by the glycerin disintegrated the microcapsule membrane. The color-producing time tended to increase as the amount of glycerin used in the soaking treatment of the microcapsules decreased. Therefore, the disintegration rate of the microcapsule membrane depended on the amount of glycerin used for the modification of the microcapsule membrane.

The effect of the amount of $FeSO_4$ in the microcapsules on the color-producing time is shown in Fig. 7. The color-producing time was longer when the amount of $FeSO_4$ in the microcapsules was increased. For example, under experimental condition F, the color-producing times of microcapsules containing 0.5, 1 and 2% $FeSO_4$ were about 46.5, 135 and 215 h, respectively. These results indicate that the moisture durability of the microcapsule membrane was improved by the increase in the proportion of crosslinking between the carboxyl group at end of the gelatin and Fe^{2+} in addition to the crosslinking presented in Fig. 3 as the amount of $FeSO_4$ in the microcapsules increased. Thus, the disintegration rate of the microcapsule membrane was thought to decrease as the amount of $FeSO_4$ added to the microcapsules increased. The amount of $FeSO_4$ in the microcapsules was also an important factor governing the control of the color-producing time.

4. Conclusions

Microcapsules containing $FeSO_4$ as the coloring agent were prepared using the interfacial polymerization reaction between gelatin and TC. The microcapsule membrane was formed by the reaction between the amino group at the end of the gelatin chain and the carbonyl group of TC. Microcapsules soaked in a 2-propanol solution of glycerin were solubilized by the adsorption of moisture and the color production by the microcapsules was caused by the reaction of $FeSO_4$ eluted from the microcapsules with the tannic acid coated on the filtration paper. The color-producing time was dependent on the amount of glycerin used in microcapsule modification and the amount of $FeSO_4$ contained in the microcapsules. The combination of paper with moisture-sensitive microcapsules prepared in this study will be able to be used to produce a new functional paper that can give information on the passage of time.

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