

Interfacial Polymerization Preparation of Functional Paper Coated with Polyamide Film Containing Volatile Essential Oil

Hideaki Ichiura,¹ Masaru Takayama,¹ Noriyoshi Nishida,² Yoshito Otani¹

¹Department of Forest Sciences, Faculty of Agriculture, Kochi University, 200 Monobe-Otsu, Nankoku, Kochi 783-8502, Japan

²Paper Ind. Res. Inst. Ehime Pref., 127 Otsu, Mendori-cho, Shikokuchuo, Ehime 799-0113, Japan

Received 16 September 2010; accepted 9 December 2010

DOI 10.1002/app.33900

Published online 4 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: An interfacial polymerization reaction was used to coat a functional paper with a polyamide film containing volatile essential oil (VEO) composites. The components of the VEO extract were linalool, α -terpineol, carveol, carvone, perillaldehyde and valencene. Preparing the polyamide film by an interfacial polymerization reaction eliminated the need for microcapsule preparation and coating with a binder, which are typically used in functional paper preparation. The interfacial polymerization involved immersing a filter paper impregnated with an

oil-in-water emulsion of ethylenediamine and VEO in a cyclohexane solution of terephthaloyl chloride. This successfully fixed the polyamide film containing the VEO on the paper surface. Release of VEO fragrance from the paper surface was studied, and the paper showed sustained release of the VEO. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 242–247, 2012

Key words: polyamides; microencapsulation; coatings; functional paper; interfacial polymerization

INTRODUCTION

Functional papers utilize the native properties of the materials they are made with, which can include adsorbent, antimicrobial, and conductive materials.^{1–8} Functional papers that release fragrance are useful in applications such as insecticide sheets, which can release an insect-repellant VEO.^{9–12} For successful application, the article needs to provide sustained release of the fragrance. Microencapsulation of the aromatic material achieves this by converting liquid VEO to a solid.^{13–15} In past studies, functional papers have usually been prepared from these microcapsules by coating them with a binder.^{15,16} This means that the preparation of functional papers with sustained fragrance release typically requires two main steps. First the microcapsules containing the VEO need to be prepared, and then they need to be coated and fixed to the paper with a binder. Consequently, a new technique is required for fixing VEO-containing microcapsules on the paper surface without the processes of microencapsulation or binder-coating.

Interfacial polymerization is step polymerization between hydrophilic and lipophilic monomers at an

oil-water interface. This type of polymerization allows the synthesis of polymers at low temperature and does not require catalysts. Thus, the interfacial polymerization technique has been applied to the preparation of microcapsules.^{17–19}

We recently investigated fixation of functional materials without microencapsulation or binder-coating processes,^{20–23} which included utilizing interfacial polymerization on a paper surface to prepare a functional paper.^{20–21} In our previous paper,²⁰ the microcapsules of a polyamide film were formed by interfacial polymerization at an oil-water interface on the paper surface. This eliminated the need for a binder to fix the microcapsules on the paper surface. We have also used interfacial polymerization to prepare a functional paper containing paraffin as phase change material, which stored thermal energy.²¹ This involved formation of an oil-in-water (O/W) emulsion of paraffin and Tween 20 in ethylenediamine (EDA) solution.

In this work, we attempted to apply this technique for preparation of a functional paper coated with a polyamide film containing orange peel VEO extract. The polyamide film-VEO coating was prepared directly on the paper surface by an interfacial polymerization reaction between ethylenediamine (EDA) and terephthaloyl chloride (TC). We characterized the polyamide film-VEO and investigated optimal conditions for its preparation. The effects of EDA solution concentration and reaction time on retention of VEO in the polyamide film were evaluated. In

Correspondence to: H. Ichiura (ichiura@kochi-u.ac.jp).

Contract grant sponsor: Ministry of Education, Science and Culture, Japan and JST, CREST.

TABLE I
Content by Percentage of Six Components in the
Volatile Essential Oil Extract from Orange Peel

Component	Content (%)
Linalool	42.3
α -Terpineol	17.0
Carveol	12.7
Carvone	16.2
Perillaldehyde	4.6
Valencene	7.2

addition, sustained release of the VEO from the polyamide film was studied. This technique facilitates production of a polyamide film on the paper surface without a binder, which provides sustained release of VEO.

EXPERIMENTAL

Materials

Polyoxyethylene sorbitan monolaurate (Tween 20), TC and dichloromethane were purchased from Wako Pure Chemical Industries, Ltd., Japan. Anhydrous EDA and cyclohexane were obtained from Kanto Chemical Co., Inc., Japan.

The VEO selected for this study was essential oil No. 9[®] (Yasuhara Chemical Co., Ltd), which is generated during production of limonene from citrus peel. The components contained in this VEO were linalool, α -terpineol, carveol, carvone, perillaldehyde, and valencene. Table I shows the percentage content of these components in the VEO extract.

Preparation of polyamide film containing VEO on the paper surface

The VEO (7.5 mL) was emulsified in an aqueous solution of 2.5–20% (w/w) EDA (15 mL) and Tween 20 (0.15 g). This mixture was agitated at 500 rpm by magnetic stirring for 5 min to yield an O/W emulsion. A filter paper (20 × 30 mm²) was immersed in and impregnated with this O/W emulsion. To perform the interfacial polymerization reaction, the filter paper was then immersed in a cyclohexane solution (10 mL) of TC (0.1 g) at room temperature for 0.5–60 min. Polymerization occurred on the paper surface at the interface between the cyclohexane-TC solution and the O/W emulsion impregnated in the paper. Following immersion, the filter paper was air-dried at room temperature for 12 h.

The preparation of the blank sheet was the following. The filter paper (20 × 30 mm²) was immersed in the O/W emulsion containing the VEO (7.5 mL), 0% EDA (15 mL) and Tween 20 (0.15 g) and was air-dried at room temperature for 12 h.

Characterization of polyamide film-VEO on the paper surface

Fourier transform infrared (FT-IR) attenuated total reflection (ATR) spectra were obtained using an FT-IR 6100 (JASCO, Inc.) spectrometer at a resolution of 4 cm⁻¹. Forty-seven scans were accumulated in the spectral range 4000–550 cm⁻¹.

The surface and cross section of the paper were analyzed by scanning electron microscopy (SEM, VE-9800, Keyence Corp.) with an accelerating voltage of 2–5 kV after osmium coating (Neoc-ST, Meiwafosis Co., Ltd.).

Evaluation of the amounts of VEO fixed on the paper

The prepared paper was immersed in 5 mL of dichloromethane at room temperature for 60 min. The solution was filtered with a membrane filter, and the concentration of VEO in a 1 μ L aliquot was analyzed by GC (GC-2014, Shimadzu) without further purification. The GC was equipped with a SLBTM-5ms column (30 m × 0.32 mm I.D., 0.25 μ m, Supelco Analytical, USA) and a flame ionization detector. The carrier gas was N₂ with a flow rate of 1.5 mL/min. The split ratio was 1 : 50. The injector port and the detector port temperatures were both 280°C. The GC oven temperature was held at 50°C for 5 min, programmed to 103°C at 3°C/min, to 250°C at 15°C/min, and held at 250°C for 10 min.

The paper remaining after extraction with dichloromethane was analyzed by pyrolyzer (PY-2020 iD, Frontier Laboratories) GC (GC-2010, Shimadzu) with a micro-jet cryo trap (MJT-1030E, Frontier Laboratories). For desorption analysis the pyrolyzer was programmed from 150 to 280°C at a rate of 50°C/min. The interface temperature of the pyrolyzer was 300°C. The GC analytical conditions were the same as those detailed above.

Evaluation of VEO release from the polyamide film formed on the paper surface

The prepared paper was placed in a 50 mL vial containing the silica-based absorptive MonoTrapTM (Rcc 18, GL sciences Co., Ltd.), and the vial was sealed with a silicon septum. The VEO released from the prepared paper over 6–96 h at 25°C was collected on the MonoTrap and extracted using dichloromethane (200 μ L) and ultrasonic extraction for 5 min. The concentration of VEO was analyzed by GC. The analysis conditions were the same as those detailed above.

After 6–96 h at 25°C, any residual VEO was extracted from the paper with 5 mL of dichloromethane at room temperature for 30 min. The concentration of VEO in the extract was analyzed using GC

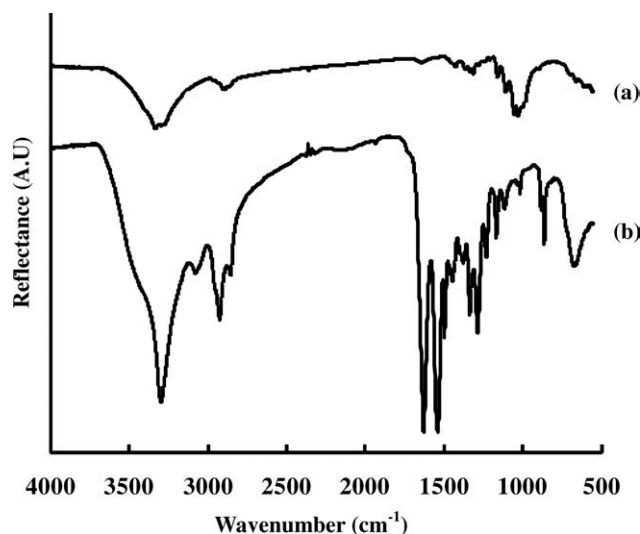


Figure 1 FT-IR spectra of (a) blank paper, and (b) the polyamide film containing the VEO prepared on the paper surface using an interfacial polymerization reaction with 10% EDA solution and a 10 min reaction time.

and the same experimental conditions as mentioned above.

The percent content of each VEO component released from the paper (REL) and of the residual VEO in the paper (RES) were evaluated according to:

$$\text{REL (\%)} = \text{REL}_1 / R_0 \times 100$$

$$\text{RES (\%)} = \text{RES}_1 / R_0 \times 100$$

where REL_1 (mg/m^2) is the amount of VEO component released from the polyamide film on the paper after 96 h, RES_1 (mg/m^2) is the amount of residual VEO component in the paper after 96 h, and R_0 (mg/m^2) is the amount of VEO component fixed on the paper.

RESULTS AND DISCUSSION

Characteristics of the polyamide film-VEO formed on the paper surface

Figure 1 shows the FT-IR spectra for the film prepared by an interfacial polymerization on the paper surface. Peaks were observed for the polyamide polymer due to a C=O stretching vibration at around 1630 cm^{-1} , a N-H bending vibration at around 1540 cm^{-1} , and a C-N stretching vibration at around 1290 cm^{-1} that was attributed to a C-N-H bond [Fig. 1(b)]. Formation of the polyamide film using interfacial polymerization was confirmed by SEM [Fig. 2(b)]. Cross-sectional SEM images of the polyamide film [Figs. 2(c,d)] indicated it only formed on the paper surface. The polyamide film was about $25 \text{ }\mu\text{m}$ thick and had a capsule-like

morphology [Fig. 2(d)]. This polyamide film was formed on the paper surface by a reaction between the EDA amino group, which was adsorbed on the paper by a physical bond, and the carbonyl group of TC. Therefore, the polyamide film was fixed on the paper by both the physical bond between the paper and the EDA, and the chemical bond between the EDA and TC.

These results show that an interfacial polymerization reaction occurred at the oil-water interface on the paper surface, which directly formed the polyamide film without the need for the two processes of microencapsulation and binder coating.

Preparation conditions for fixation of VEO on the paper surface using an interfacial polymerization reaction

The effect of the EDA concentration on total R_0 of the polyamide film prepared on the paper surface was investigated with a reaction time of 10 min (Fig. 3). The total R_0 was defined as the total amount of the six components fixed on the paper.

The amounts of VEO fixation was increased with increasing the concentration of EDA. We reported that the thickness of the polyamide film prepared on the paper surface increased with an increasing EDA concentration.²⁰ As the thickness of the polyamide film prepared on the paper surface increased, the amount of the VEO fixed on paper surface increased. The fixation of the VEO was thought to be caused by the formation of polyamide film. The optimal concentration of EDA was 10%, which gave maximum total R_0 and securely fixed the polyamide film to the paper surface. These results show that the polyamide film containing the VEO could be directly formed on the paper surface by the interfacial polymerization. It was thought the VEO was fixed by the capsule-like morphology of the polyamide film [Fig. 2(d)]. In contrast, with 20% EDA solution the total R_0 was much lower, which indicates the polyamide film was detached from the paper surface. We reported that fixation of the polyamide film on the paper surface was found to be difficult when the thickness of the polyamide film formed on the paper surface by interfacial polymerization was reached about over $25 \text{ }\mu\text{m}$.²⁰ This indicates the EDA concentration is an important factor for the fixation of the polyamide film.

The effect of the reaction time on the total R_0 was investigated with an EDA concentration of 10% (Fig. 4). The reaction time was defined as the time of immersion in the cyclohexane solution of TC. A reaction time of 10 min was optimal and gave maximum total R_0 for the polyamide film. However, when the reaction time was more than 10 min, the total R_0 of the prepared paper decreased. The VEO

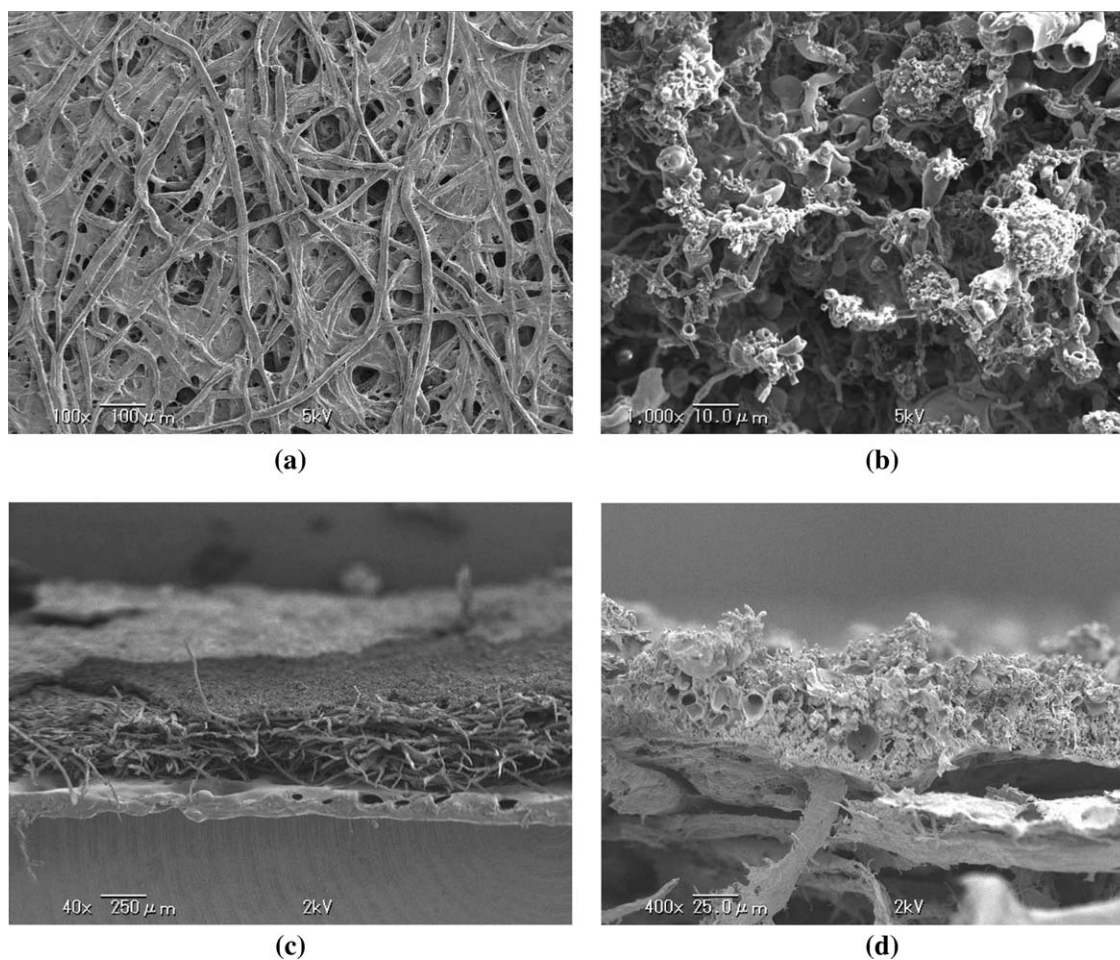


Figure 2 SEM images of (a) blank paper, and (b) the polyamide film prepared on the paper surface by an interfacial polymerization reaction, (c) and (d) the cross section of the polyamide film prepared on the paper surface. Experimental conditions: 10% EDA solution, and 10 min reaction time.

fixed on the filter paper was thought to gradually leach out into the cyclohexane phase as the reaction time increased.

A polyamide film was prepared on the paper surface using the optimal conditions of 10% EDA and 10 min reaction time. The R_0 values of this film were

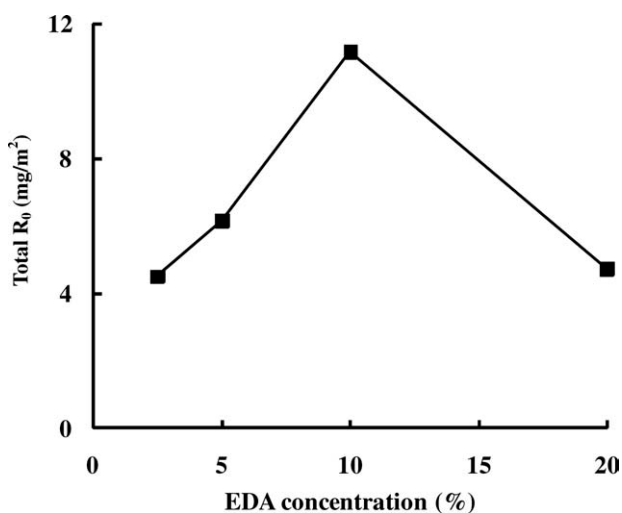


Figure 3 Effect of the EDA concentration on total R_0 . Experimental conditions: 2.5–20% EDA solution and 10 min reaction time.

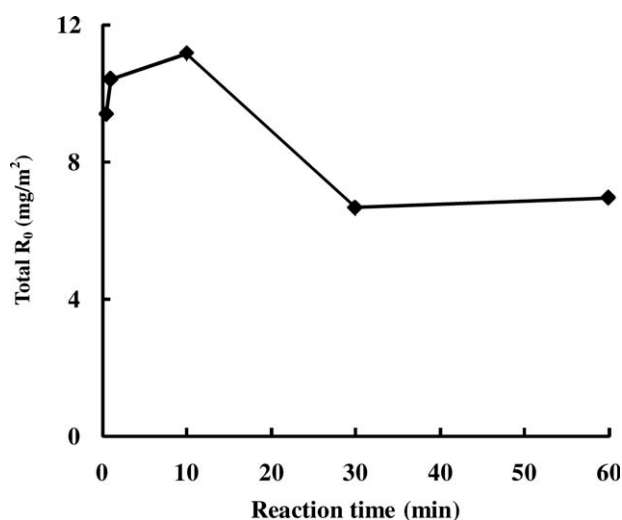


Figure 4 Effect of reaction time on total R_0 . Experimental conditions: 10% EDA solution.

TABLE II
Amount of Each VEO Component (R_0) Which Adhered to the Prepared Functional Paper and the Blank Paper^a

Component	R_0 prepared paper ^a (mg/m ²)	R_0 blank paper (mg/m ²)
Linalool	3.13	9.78
α -Terpineol	2.13	3.90
Carveol	2.24	2.99
Carvone	1.29	3.62
Perillaldehyde	0.77	0.68
Valencene	1.58	1.71
Total	11.15	22.68

^a Experimental conditions: Prepared sheet; 10 % EDA solution, and 10 min reaction time. Blank paper; 0 % EDA solution, and 10 min reaction time.

measured and compared with that of a blank paper (Table II). Fixation of the VEO to the blank paper was by physical adsorption. The total R_0 of the blank paper was 22.68 mg/m² and higher than that of the prepared functional paper. In comparison to the blank paper, smaller interspaces formed by the polyamide film were available for VEO adsorption and fixation on the prepared paper surface. These results indicate that the VEO was fixed, not by the filter paper, but by the polyamide film formed on the paper surface by interfacial polymerization.

The prepared paper was extracted with dichloromethane and analyzed by pyrolyzer-GC for residual VEO. The six component peaks identified in this study, which were linalool (RT: 33.9 min), α -terpineol (RT: 40.3 min), carveol (RT: 41.2 min), carvone (RT: 43.3 min), perillaldehyde (RT: 43.8 min) and valencene (RT: 46.4 min), disappeared after the extraction. Thus, the extraction method in this study was sufficient to analyze the amounts of the VEO fixed on the paper surface.

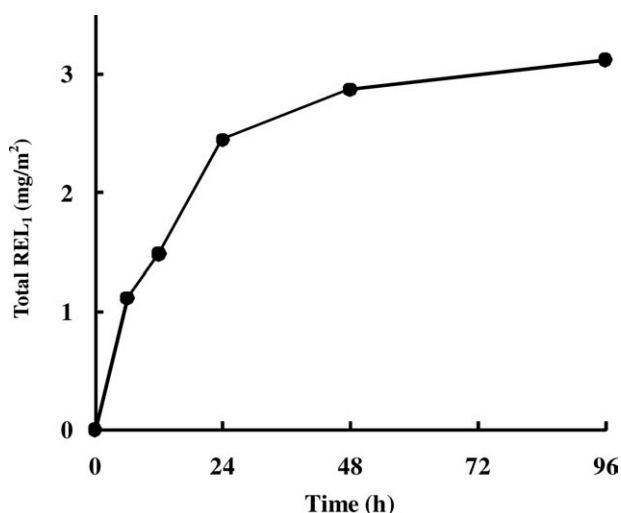


Figure 5 Total REL₁ of polyamide film prepared on the paper surface. Experimental conditions: 10% EDA solution, and 10-min reaction time.

TABLE III
Amount of Each VEO Component Released from the Polyamide Film (REL₁) and Percent Released (REL) of the Prepared Paper^a After 96 h

Component	REL ₁ (mg/m ²)	REL (%)
Linalool	0.87	25.54
α -Terpineol	0.56	25.20
Carveol	0.54	25.15
Carvone	0.38	26.24
Perillaldehyde	0.17	35.49
Valencene	0.60	31.38
Total	3.12	28.0

^a Experimental conditions: 10 % EDA solution, and 10 min reaction time.

Release of VEO from the polyamide film

Figure 5 shows temporal changes of total REL₁. The total REL₁, which is defined as the total amount of six components released from the polyamide film, increased over time. We observed the release of each of the six components in the VEO from the polyamide film. The REL₁ values of linalool, α -terpineol, carveol, carvone, perillaldehyde and valencene for the prepared paper after 96 h were 0.87, 0.56, 0.54, 0.38, 0.17, and 0.60 mg/m², respectively, (Table III). The total REL after 96 h was about 28% (Table III). This confirmed the release of the six components from the polyamide film. Okahata and coworkers reported that polyamide film prepared from EDA and TC had a porous structure,¹⁸ which would facilitate release of the VEO from the prepared film in this study.

The total R_0 of the prepared paper was lower than that of the blank paper (Table II). However, the total RES of the prepared paper decreased at a slower speed than that of the blank paper (Fig. 6). Total

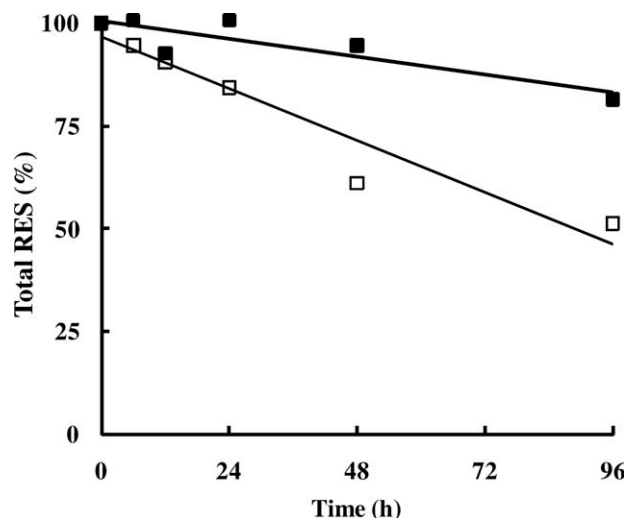


Figure 6 Total RES of (□) blank paper and (■) paper prepared by interfacial polymerization. Experimental conditions: 10% EDA solution, and 10-min reaction time.

TABLE IV
Amount of Residual VEO Component in the Paper (RES₁) and Percent Remaining (RES) of the Prepared Paper^a and Blank Paper After 96 h

Component	Prepared paper		Blank paper	
	RES ₁ (mg/m ²)	RES (%)	RES ₁ (mg/m ²)	RES (%)
Linalool	2.70	86.4	4.30	44.0
α-Terpineol	1.70	79.6	2.26	5.79
Carveol	1.92	85.4	1.81	60.5
Carvone	0.97	75.3	2.04	56.4
Perillaldehyde	0.62	80.2	0.36	52.7
Valencene	1.17	73.9	0.85	49.7
Total	9.08	81.5	11.62	51.2

^a Experimental conditions: 10 % EDA solution, and 10 min reaction time.

RES was defined as the sum percentage of the residual amounts of the six components remaining in the polyamide film after 96 h. Total RES of the prepared paper was 81.5%, and was higher than that of the blank paper after 96 h (Table IV). These results suggest the blank paper without polyamide film could not provide sustained release of the VEO. In contrast, the functional paper coated with polyamide film by interfacial polymerization could control the release of the VEO from the paper and provide sustained release. The RES values of each of the six components of the prepared paper were also higher than those of the blank paper. The RES of linalool fixed on the prepared paper was particularly high as linalool has the lowest boiling point of the six components. Interfacial polymerization preparation of the polyamide film on the paper eliminated the need for microencapsulation and a binder, and provided a higher function for sustained release of the VEO than the blank paper. These results indicate that this technique was effective for producing a paper capable of sustained release of the VEO.

CONCLUSIONS

Polyamide film containing VEO was prepared on the surface of a filter paper by an interfacial polymerization reaction between EDA and TC at the oil-water interface on the paper surface. The amount of the VEO fixed on the paper depended on the concentration of EDA and the reaction time. The optimum concentration of EDA was 10% and the optimum reaction time was 10 min.

VEO was released from the polyamide film on the paper surface. The total RES of the prepared paper after 96 h was higher than that of the blank paper. This indicated that the VEO was released in a sustained manner. Preparation of the polyamide film directly on the paper surface without microencapsulation or binder coating processes successfully produced a functional paper that was capable of sustained release of the VEO. This technique will be useful in the preparation of functional papers that emit fragrance.

References

- Matsubara, H.; Takada, M.; Koyama, S.; Hashimoto, K.; Fujishima, A. *Chem Lett* 1995, 24, 767.
- Iguchi, Y.; Ichiura, H.; Kitaoka, T.; Tanaka, H. *Chemosphere* 2003, 53, 1193.
- Ichiura, H.; Kitaoka, T.; Tanaka, H. *J Mater Sci* 2002, 37, 2937.
- Fukahori, S.; Iguchi, Y.; Ichiura, H.; Kitaoka, T.; Tanaka, H.; Wariishi, H. *Chemosphere* 2007, 66, 2136.
- Fukahori, S.; Ichiura, H.; Kitaoka, T.; Tanaka, H.; Wariishi, H. *J Mater Sci* 2007, 42, 6087.
- Ichiura, H.; Kitaoka, T.; Tanaka, H. *Chemosphere* 2003, 51, 855.
- Ichiura, H.; Kitaoka, T.; Tanaka, H. *J Mater Sci* 2003, 38, 1611.
- Fukahori, S.; Ichiura, H.; Kitaoka, T.; Tanaka, H. *Environ Sci Tech* 2003, 37, 1048.
- Takahashi, T.; Taguchi, Y.; Tanaka, M. *J Chem Eng Japan* 2005, 38, 929.
- Abdel-Mohdy, A. F.; Fouda, M.-G. M.; Rehan, F. F.; Ali, S. A. *J Textile Inst* 2009, 100, 695.
- Takahashi, T.; Taguchi, Y.; Tanaka, M. *J Appl Polym Sci* 2000, 77, 107.
- Hirech, K.; Payan, S.; Carnelle, G.; Brujes, L.; Legrand, J. *Powder Tech* 2003, 130, 324.
- Ishi, R.; Imai, Y.; Wada, M.; Ebina, T.; Hanaoka, T.; Miaukami, F. *Appl Clay Sci* 2006, 33, 99.
- Rodrigues, S. N.; Martins, I. M.; Fernandes, I. P.; Gomes, P. B.; Mata, V. G.; Barreiro, M. F.; Rodrigues, A. E. *Chem Eng J* 2009, 149, 463.
- Rodrigues, S. N.; Fernandes, I. I.; Martins, M.; Mata, V. G.; Barreiro, F.; Rodrigues, A. N. *Ind Eng Chem Res* 2008, 47, 4142.
- Ichimura, K. *Development of Chromic Materials*; CMC Publishing Co.: Ltd.: Japan, 2000; p 253–261 (in Japanese).
- Ichiura, H.; Morikawa, M.; Fujiwara, K. *J Mater Sci* 2005, 40, 1987.
- Okahata, Y.; Lim, H.-J.; Nakamura, G.; Hachiya, S. *J Am Chem Soc* 1983, 105, 4855.
- Park, S.-J.; Shin, Y.-S.; Lee, J.-R. *J Colloid Inter Sci* 2001, 241, 502.
- Ichiura, H.; Morikawa, M.; Ninomiya, J. *J Mater Sci* 2006, 41, 7019.
- Ichiura, H.; Ohi, T.; Oyama, H.; Yokota, H.; Kunitake, T.; Ohashi, S.; Morikawa, M. *J Mater Sci* 2008, 43, 1486.
- Ichiura, H.; Konishi, T.; Morikawa, M. *J Mater Sci* 2009, 44, 992.
- Ichiura, H.; Kaneda, Y.; Ohtani, H. *J Mater Sci* 2010, 45, 1343.