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Low temperature-dependence of N,N-dimethyl-3-methylbenzamide (DEET) release from a functional paper containing paraffin–DEET composites prepared using interfacial polymerization

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HIGHLIGHTS

- We prepared a polyamide paper coating containing paraffin–DEET composites.
- The polyamide film was directly prepared using interfacial polymerization.
- The functional paper containing paraffin released DEET for a long period.
- DEET release from the functional paper had a low temperature dependence.
- Paraffin was important in achieving the sustained release of DEET.

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ABSTRACT

An interfacial polymerization reaction was used to prepare a functional paper with a polyamide film containing paraffin–N,N-dimethyl-3-methylbenzamide (DEET) composites, which gave a sustained release of DEET with a low temperature dependence. Preparing the polyamide film using an interfacial polymerization reaction eliminated the need for preparing microcapsules and coating the paper with a binder, which is the typical functional paper preparation method. Filter paper impregnated with an oil–water emulsion (composed of ethylenediamine and paraffin microcapsules prepared using methyl methacrylate polymer) was left in a beaker containing a cyclohexane solution of terephthaloyl chloride. The polyamide film containing paraffin–DEET composites could attach itself to the treated paper surface. We studied the release of DEET from the paper with and without paraffin, and its temperature dependence. The functional paper with paraffin showed the sustained release of DEET at high temperatures, but the release was usually inefficient. However, the sustained release of DEET was not temperature dependent, and this was found to be caused by the release of DEET being controlled by the paraffin melting. The optimum paraffin/DEET ratio was 9:1, taking into consideration the amount of DEET released from the paper and the low temperature dependence of the sustained release of DEET.

1. Introduction

Microcapsules are useful for the long-term protection of functional materials from environmental factors, for controlling the release of specific materials, and for converting liquids into the solid state [1–3]. We have studied functional papers, which make use of the native properties of the materials they are made with, and these materials can include adsorbents, antimicrobial agents, and conductive materials [4–12]. Functional papers that release fragrances are useful in applications such as insecticide sheets [12,13], which can release, for example, the insect repellant N,N-dimethyl-3-methylbenzamide (DEET) [14–17], which is the focus of the work presented here. DEET is a popular insect repellent because of its high efficiency and safety. Materials containing DEET are applied to products to repel biting insects. Successful application in our study was defined as the treated paper providing the long-lasting release of DEET.

We have recently investigated fixing functional materials without either microencapsulation or binder-coating processes [12,13,18–22], including preparing functional paper using interfacial polymerization on the paper surface [12,19–21]. This technique will be useful for preparing functional papers that emit DEET. In a previous paper [12], we described the preparation of a

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polyamide film containing a volatile essential oil (VEO) on the surface of a filter paper using an interfacial polymerization reaction between ethylenediamine (EDA) and terephthaloyl chloride (TC) at the oil–water interface. The residual VEO concentrations in the paper prepared were higher after 96 h than the VEO concentrations in blank paper. This indicated that the VEO was released in a sustained manner. However, the amounts of VEO released from the paper, or the residual VEO in the paper, changed dramatically depending on the ambient temperature. In other words, the amount of VEO released from the paper increased with increasing temperature, and the amount of residual VEO in the paper at a specific time decreased with increasing temperature. The release of DEET from a functional paper will need to have a low temperature dependence to achieve the efficient and consistent release of DEET over a long period. Therefore, we attempted to prepare a functional paper that would release DEET with a low temperature dependence by incorporating paraffin.

Paraffin with a solid–liquid phase change at a specific temperature has been widely used as a phase change material, and it has been used for thermal energy storage because of its large heat storage capacity, good thermal characteristics, low vapor pressure when melted, and chemical stability [23–26]. Paraffin is in the solid state below its melting point, and it is in the liquid state above its melting point. In the study presented here, we prepared functional paper containing paraffin–DEET composites using an interfacial polymerization reaction on the paper surface. The release of DEET from the functional paper will be controlled by the melting of the paraffin in the functional paper containing the paraffin–DEET composites when the temperature is higher than the melting point of the paraffin. The release of DEET from the functional paper can, therefore, be controlled by the paraffin used. The paraffin used in this study is important in achieving the low temperature dependence of the DEET release from the paper.

In the study presented here, the paraffin–DEET composites were encapsulated using a polymer membrane formed from poly (methyl methacrylate) (PMMA) [27] to improve the affinity of the paraffin for the paper [21]. Once this was achieved, the interfacial polymerization technique, which is a polymerization reaction between EDA and TC on the paper surface, was applied to prepare the functional paper containing the paraffin–DEET composites. This technique allows a polyamide film containing the paraffin–DEET composites on the paper surface to be produced without the need for a binder. The properties of the paper containing the paraffin–DEET composites are presented here, and the optimal conditions for its preparation were determined. We investigated the effect of the paraffin to DEET ratio in the composites on the temperature dependence of DEET release from the paper.

2. Materials and methods

2.1. Materials

Polyoxyethylene sorbitan monolaurate (Tween 20), methyl methacrylate monomer (MMA), 2,2′-azobis(2,4-dimethyl valeronitrile) (V-65), and DEET were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Anhydrous EDA, cyclohexane, and paraffin (m.p. about 42–44 °C) were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). TC was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan).

2.2. Preparation of functional paper with paraffin–DEET composites on the paper surface

V-65 (0.2 g), used as an azo initiator, was dissolved in melted paraffin (0 or 1–9.99 mL) at 60 °C. DEET (0.01–9 mL) and MMA (8 mL) were poured into an aqueous solution of 2.5% (w/w) EDA (15 mL), 1 M NaOH (15 mL), and Tween 20 (0.5 g), which acted as an emulsifier. Table 1 shows the compositions of the mixtures used for each paraffin–DEET composite tested on the functional paper. The paraffin and aqueous mixtures were mixed together at 500 rpm with a magnetic stirrer for 10 min at 60 °C to prepare an oil–water (O/W) emulsion. The paraffin–DEET composites prepared this way became encapsulated within PMMA. Filter papers (No. 2; Toyo Rosi Kaisha Ltd., Tokyo, Japan) were impregnated with the O/W emulsion containing the paraffin–DEET composite microcapsules and then immersed in a cyclohexane solution (10 mL) of TC (0.1 g) at 25 °C for 10 min, then air-dried at room temperature for 12 h. The functional papers containing paraffin–DEET were stored in 50 mL vials at 4 °C.

2.3. Characterization of paraffin–DEET composites on the paper surface

Fourier transform infrared (FT-IR) spectra were measured using an FT-IR-6100 instrument (JASCO Inc., Tokyo, Japan) using attenuated total reflection at a resolution of 4 cm^{-1} throughout the spectral range (4000–550 cm^{-1}), with an accumulation of 40 scans.

The paper surfaces were analyzed using scanning electron microscopy (SEM; VE-9800 instrument; Keyence Corporation, Osaka, Japan), with an accelerating voltage of 5 kV, after they had been treated with an osmium coating (Neoc-ST; Meiwafosis Co., Ltd., Tokyo, Japan).

The latent heat of the paraffin in the paper prepared was measured using a differential scanning calorimeter (DSC; DSC3200SA instrument; Bruker AXS K.K., Kanagawa, Japan). The DSC analysis was performed over the temperature range 10–150 °C, with a heating rate of 15 °C/min.

The tensile strength of the paper prepared using the interfacial polymerization method was determined using a tensile tester (STB; A&D Co., Ltd., Tokyo, Japan). The specimens tested were 20 × 30 mm, and the test speed and span distance were 20 mm/min and 20 mm, respectively.

The wet tensile strength of the functional paper containing paraffin–DEET composites was also measured. A functional paper was dipped in distilled water for 1 min, excess water was removed, then the tensile strength was measured immediately using the tensile strength test method described above.

The water contact angle on the functional paper was measured using a static sessile drop at room temperature. The measurements were performed immediately after drops of water had formed on the surface of the functional paper containing paraffin–DEET composites, using a DM-500 instrument (Kyowa Interface Science Co., Ltd., Saitama, Japan). The contact angle was recorded after 1 s.

2.4. Evaluating the amount of DEET fixed onto the paper

The amount of DEET fixed to the functional paper was evaluated immediately after the paper was prepared.

The DEET in a prepared paper was extracted by immersing the paper in ethanol (3 mL) and placing it in an ultrasonication instrument for 5 min. The solution was filtered through a membrane filter and the DEET concentration in a 1 μL aliquot was analyzed by high performance liquid chromatography (HPLC; LC-20AD instrument; Shimadzu Corporation, Kyoto, Japan) without further purification. The HPLC instrument was equipped with a C_{18} column (Kinetex 2.6 μm C18, 150 mm long, 4.6 mm id; Phenomenex, Torrance, CA, USA) and a UV detector (recording the absorbance at 254 nm). The mobile phase was 70% (v/v) acetonitrile and 30% (v/v) distilled water, and it was used at a constant flow rate of 1.0 mL/min. The column temperature was 40 °C.