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Paper–paraffin composites prepared by interfacial polymerisation reaction on paper surface and its function of thermal energy storage

**Hideaki Ichiura · Tatsuo Ohi · Hiroshi Oyama ·
Hiroshi Yokota · Tetsunori Kunitake ·
Shunpei Ohashi · Masaaki Morikawa**

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Abstract Paper–paraffin composites were prepared by an interfacial polymerisation reaction on the paper surface and its function of thermal energy storage was studied. Filter paper impregnated with O/W emulsion, which was composed of ethylenediamine, NaOH and paraffin microcapsules prepared by methyl methacrylate polymer (PMMA), was left in a beaker containing a cyclohexane solution of terephthaloyl chloride. The paraffin could fix on the treated paper surface and the encapsulation of the paraffin before the interfacial polymerisation reaction on the paper surface was effective in the preparation of paper with the function of heat storage.

Introduction

Thermal energy storage has been used in many applications, such as buildings, textiles, clothing and the thermal protection of food [1–2]. Thermal energy storage systems have used the latent heat of phase change materials [1–8], and these systems have high-energy storage density and capacity. Phase change materials (PCMs) store heat by a phase change corresponding to a phase transition temperature. Paraffin with a solid–liquid phase change has been widely used as a PCM and has been applied in thermal energy storage because of its large heat storage capacity, proper thermal characteristics, low vapour pressure in the melt and chemical stability [4–8].

In this study, a composite material of functional paper containing paraffin as the PCM was prepared for thermal energy storage. Functional paper is a composite material made with paper composed of cellulose fiber and a functional material, such as an adsorbent, antimicrobial or conductive material [9–11]. Functional paper utilises the native properties of the materials present in the paper. The functional paper prepared in this study was made of paper and paraffin, which has usually been prepared by coating the paraffin microcapsules with a binder [12]. However, in our previous article [13], a nylon film was formed at the oil–water interface formed on the paper surface using an interfacial polymerisation technique such that it could be expected to fix on the paper surface without the need of a binder. In this work, the interfacial polymerisation technique was applied to prepare nylon film involving paraffin directly on a paper surface. However, paper composed of cellulose fiber with hydrophilicity lacks an affinity for the paraffin with hydrophobicity. When the interfacial polymerisation technique is applied in the preparation of the functional paper containing paraffin, it is supposed that the paraffin cannot fix on the paper surface. Thus, in this study it is important to solve the above problem for the preparation of functional paper containing paraffin using the interfacial polymerisation technique.

H. Ichiura (✉)
Faculty of Agriculture, Kochi University, 200 Monobe-Otsu,
Nankoku-shi 783-8502, Japan
e-mail: ichiura@kochi-u.ac.jp

T. Ohi · H. Oyama
Kami Shoji Co., Ltd., 1-2-27 Miyagawa, Mishima,
Shikokuchuo-shi 799-0404, Japan

H. Yokota · T. Kunitake
Ehime Paper Co., Ltd., 370 Muramatsu-cho, Shikokuchuo-shi
799-0401, Japan

S. Ohashi · M. Morikawa
Paper Ind. Res. Inst. Ehime Pref., 127 Otsu, Doiyama,
Mendori-cho, Shikokuchuo-shi, Ehime 799-0113, Japan

In this report, the encapsulation of paraffin using a polymer membrane formed from poly (methyl methacrylate) (PMMA) [14] as a pre-treatment was performed to improve the affinity of the paraffin on the paper, after which the interfacial polymerisation technique, which is a polymerisation reaction between ethylenediamine and terephthaloyl chloride on the paper surface, is applied to prepare the paper–paraffin composites with thermal energy storage.

Suitable conditions were investigated for the fixation and formation of nylon film involving paraffin on the paper surface using the interfacial polymerisation technique reported in the previous article. The effect of the amount of paraffin addition and reaction time on the latent heat of fusion was also studied.

Experimental section

Materials

NaOH, polyoxyethylene sorbitan monolaurate (Tween 20), terephthaloyl chloride (TC), methyl methacrylate and 2,2′-Azobis (2,4-dimethyl valeronitrile) (V-65) were purchased from Wako Pure Chemical Industries, Ltd., Japan, and anhydrous ethylenediamine (ED), cyclohexane and paraffin (m.p. about 42–44 °C) were obtained from Kanto Chemical Co., Inc., Japan.

Preparation of paper–paraffin composites by the interfacial polymerisation technique

Three methods (samples 1, 2 and 3) of preparation for functional paper containing paraffin were performed. The methods are illustrated in Fig. 1.

Preparation of sample 1

Filter paper (Toyo Roshi Kaisha, Ltd., NO. 2) impregnated with TC (0.1 g) dissolved by paraffin solution (5 g) melted at 50 °C was immersed in an aqueous mixed solution of 2.5% (w/w) ED (5 mL) and 1N NaOH (5 mL) at 4 °C for 720 min, after which the filter paper was air-dried at room temperature.

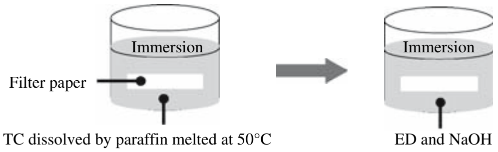
Preparation of sample 2

The paraffin solution (5 g) melted at 50 °C was poured into an aqueous solution of 2.5% (w/w) ED (15 mL), 1N NaOH (15 mL) and 1% (w/v) Tween 20 (0.3 g) as an emulsifier. This mixture was agitated at 500 rpm by magnetic stirring for 10 min at 50 °C and an O/W emulsion was prepared. The filter paper impregnated with this O/W emulsion was immersed in cyclohexane solution (20 mL) of TC (0.2 g) at 4 °C for 720 min, after which the filter paper was air-dried at room temperature.

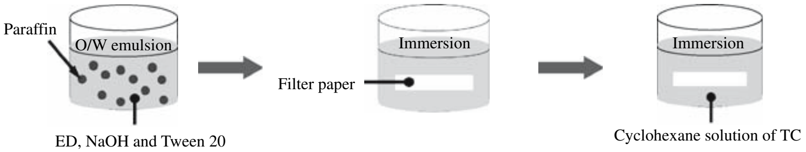
Preparation of sample 3

V-65 (on paraffin 67%; 3.6–21.6 mL) as an azo initiator dissolved by paraffin solution (5–30 g) melted at 50 °C and methyl methacrylate monomer (on paraffin 2%; 0.1–0.6 g) were poured into an aqueous solution of 2.5% (w/w) ED (15 mL), 1N NaOH (15 mL) and 1% (w/v) Tween 20 (0.3 g) as an emulsifier. This mixture was agitated at 500 rpm by magnetic stirring for 10 min at 50 °C and an O/W emulsion was prepared. The paraffin was encapsulated by PMMA. The filter paper impregnated with the O/W

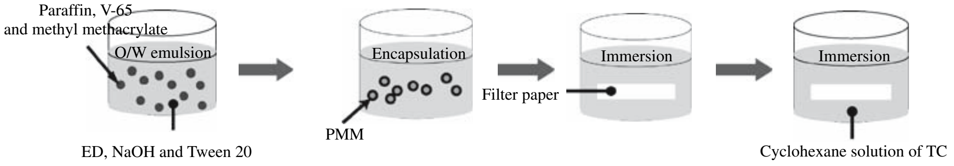
Fig. 1 Illustration of the preparation of samples 1, 2 and 3



(a) Preparation of Sample 1



(b) Preparation of Sample 2



(c) Preparation of Sample 3

emulsion containing the paraffin microcapsule was immersed in cyclohexane solution (20 mL) of TC (0.2 g) at 4 °C for a reaction time of 1–720 min, and was air-dried at room temperature.

Characterization of samples 1, 2 and 3

Fourier transform infrared (FT-IR) spectra were measured with a FT-IR-480 (JASCO, Inc.) using attenuated total reflection (ATR) at a resolution of 4 cm^{-1} throughout the spectral range (4,000–700 cm^{-1}) and an accumulation of 100 scans. The paper surfaces of samples 1, 2 and 3 were analysed by scanning electron microscopy (SEM, JSM-5510LV, JEOL Inc.) with an accelerating voltage of 15 kV after Pt coating.

The latent heats of the samples were measured with a differential scanning calorimeter (DSC, EXSTAR 6000, Seiko Instruments Inc.). DSC thermal analysis was performed in the temperature range of 10–150 °C with heating rates of 15 °C/min. The sample weight was 65 mg. The latent heats of fusion of the samples were determined by numerical integration of the area under the peaks that represent the solid–liquid phase transition.

Results and discussion

Preparation conditions for the paraffin fixation on the paper surface using the interfacial polymerisation technique

Figure 2 shows the FT-IR spectrum and SEM images of the filter paper of sample 1. As shown in Fig. 2a, peaks attributed to the nylon polymer (around 1,630 cm^{-1}, 1,545 cm^{-1} and 1,290 cm^{-1}) were not confirmed and the spectrum of sample 1 was the same as that of the filter paper. Additionally, the formation of the nylon film on the paper surface could not be observed in the SEM image. It was supposed that paraffin solution containing TC with hydrophobicity could not fix on the paper surface because of the cellulose fiber with hydrophilicity and thus nylon film, which was prepared by a reaction between ED and TC, could not form on the paper surface via the interfacial polymerisation technique. The fixation of the paraffin solution containing TC with hydrophobicity on the paper surface with hydrophilicity was shown to be difficult.

For sample 2, the functional paper containing the paraffin was prepared by the interfacial polymerisation reaction on the paper surface after the formation of an O/W emulsion by the addition of Tween 20 to the mixture of the ED solution to improve the affinity of the paraffin on the paper.

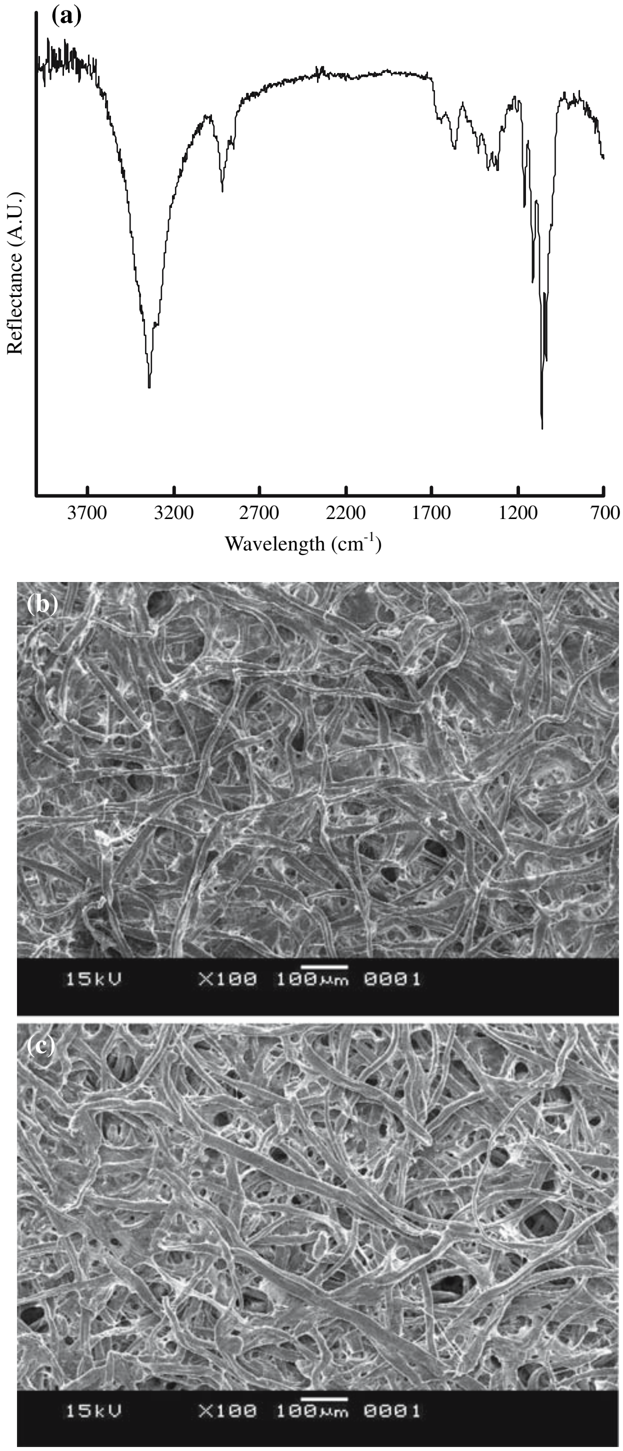
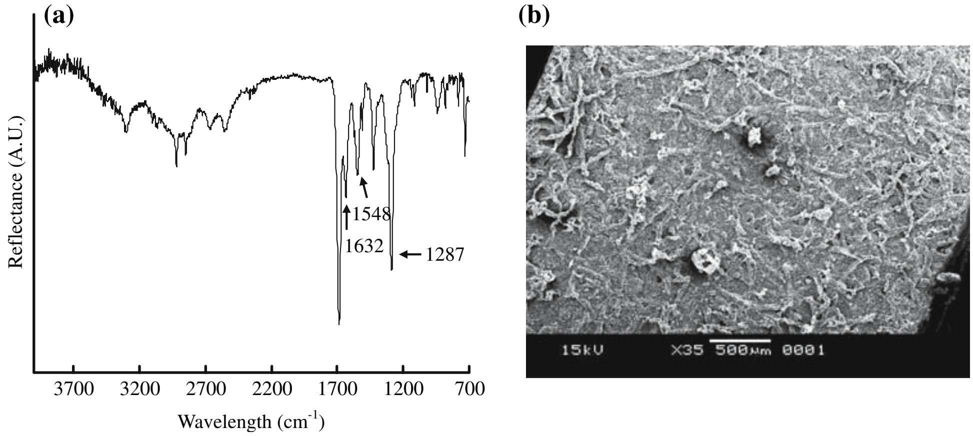


Fig. 2 FT-IR spectra (**a**) of sample 1, and SEM images of (**b**) filter paper and (**c**) sample 1

Figure 3a and b shows the FT-IR spectrum and SEM image of sample 2, respectively. In the FT-IR spectrum of sample 2, three characteristic peaks (about 1,630 cm^{-1}, 1,545 cm^{-1} and 1,290 cm^{-1}) were observed as shown in Fig. 3a. These were attributed to polyamide and, thus,

Fig. 3 FT-IR spectra (**a**) and SEM image (**b**) of sample 2



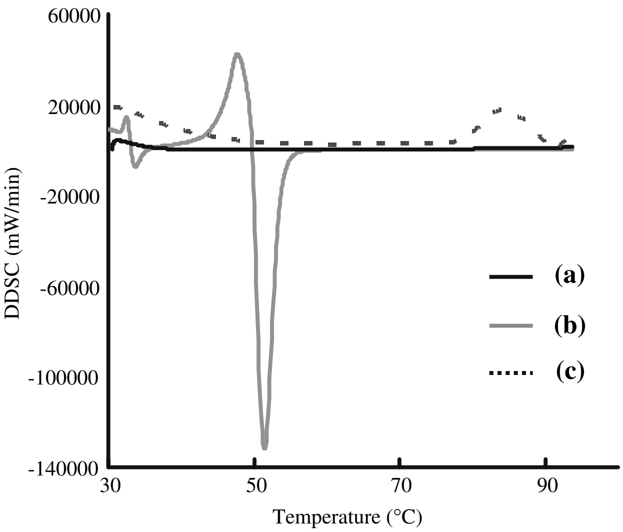


Fig. 4 DSC analyses of sample 2 (**a**), pure paraffin (**b**) and nylon film prepared on a paper surface using interfacial polymerisation without paraffin (**c**)

nylon film on the paper surface was successfully prepared by the interfacial polymerisation reaction on the paper surface. The formation of the nylon film on the paper surface was also confirmed by SEM (Fig. 3b). However, as shown in Fig. 4a, the peak around 50 °C attributed to the paraffin (Fig. 4b) could not be observed in DSC analysis. This result was the same for as the nylon film prepared using the interfacial polymerisation without paraffin, as shown in Fig. 4c. These results indicate that the paraffin could not fix on the paper surface because the paraffin with hydrophobicity leaked from the paper surface to the cyclohexane solution of TC during the interfacial polymerisation reaction on the paper surface. Thus, not only was there an improvement in the affinity of the paper on the paraffin but prevention of paraffin leakage from the paper surface during the interfacial polymerisation reaction was also thought to be an important factor.

Sample 3 was prepared by interfacial polymerisation on the paper surface after the encapsulation of the paraffin by PMMA [14]. The average diameter of the paraffin microcapsule was about 1.05 μm.

Figure 5 shows the FT-IR spectrum and SEM images of sample 3, which was prepared by the addition of 5 g paraffin and the reaction time of 720 min. The peaks of the nylon polymer due to a C=O stretching vibration at around 1,633 cm^{-1}, an N–H bending vibration at around 1,546 cm^{-1} and a C–N stretching vibration at around 1,291 cm^{-1}, attributed to a C–N–H bond, were observed as shown in Fig. 5a. Similarly, SEM image in Fig. 5b shows the formation of the nylon film. In addition, Fig. 5c shows that the paraffin microcapsules formed by the interfacial polymerisation technique were fixed on the paper surface. In the DSC thermogram of sample 3, as shown in Fig. 6, the peak due to paraffin at around 50 °C was confirmed and the paraffin can fix on the paper surface by the interfacial polymerisation reaction after the encapsulation of the paraffin by PMMA. The paraffin encapsulation by PMMA caused a decrease of the amount of paraffin leakage through the nylon film, which had the porous structure [15], during the interfacial polymerisation reaction. Therefore, the encapsulation of paraffin by PMMA before applying the interfacial polymerisation technique prevented paraffin leakage from the paper surface during the interfacial polymerisation reaction.

These results show that the encapsulation of the paraffin before the interfacial polymerisation avoided paraffin leakage from the paper surface and caused the direct formation on the paper surface of nylon film involving the paraffin without requiring the use of a binder.

Effects of the amount of paraffin and reaction time on the latent heat of fusion

In this section, sample 3 was used as the experimental specimen and the effects of the amount of the paraffin

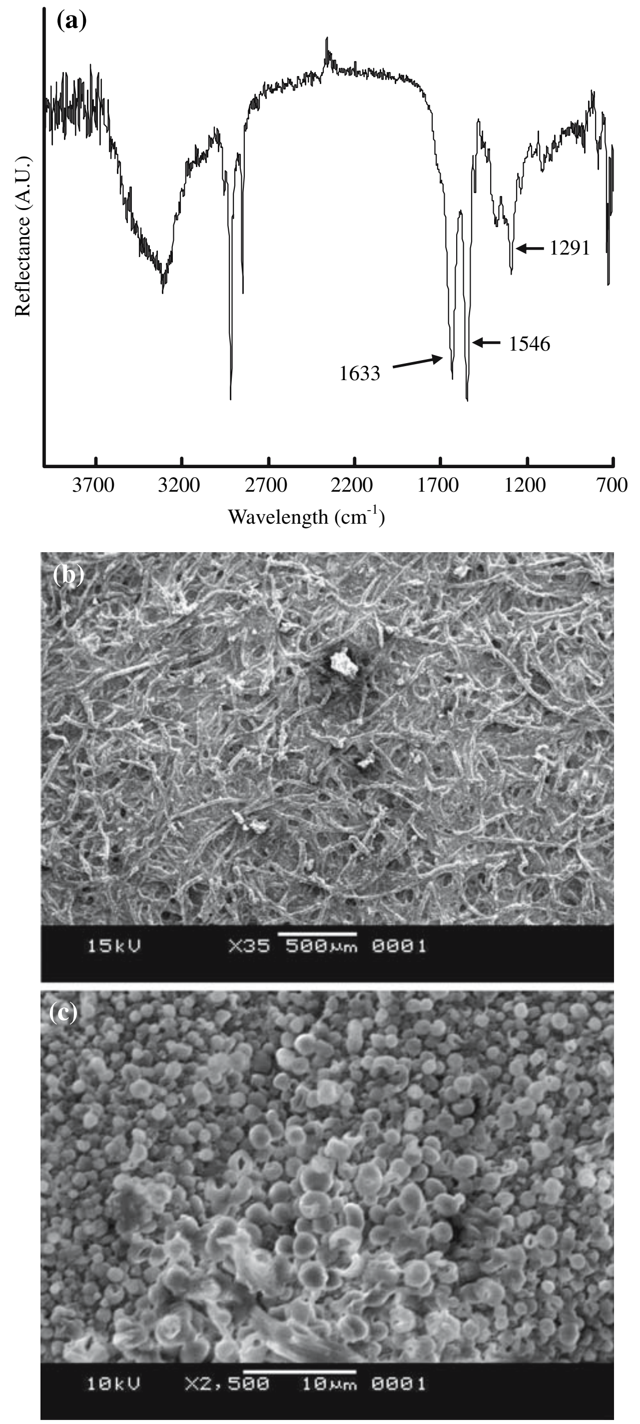


Fig. 5 FT-IR spectra (**a**) of sample 3, and SEM image (**b**) and (**c**) of sample 3, experimental conditions (**b**): paraffin, 5 g; reaction time, 720 min; (**c**): paraffin, 30 g; reaction time, 720 min

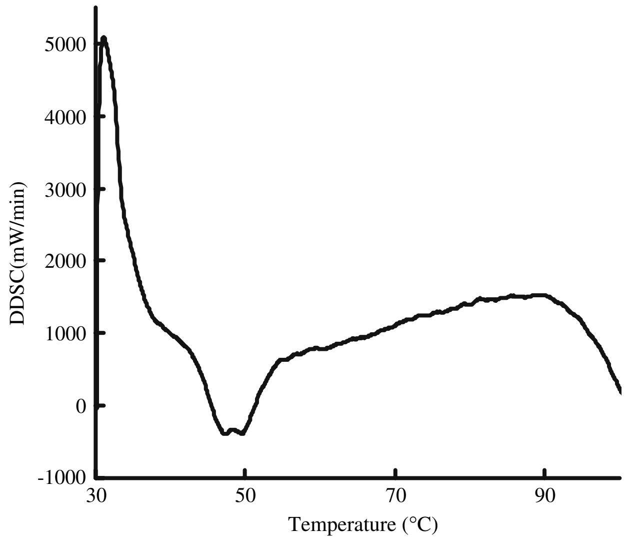


Fig. 6 DSC analysis of sample 3, experimental conditions: paraffin, 5 g; reaction time, 720 min

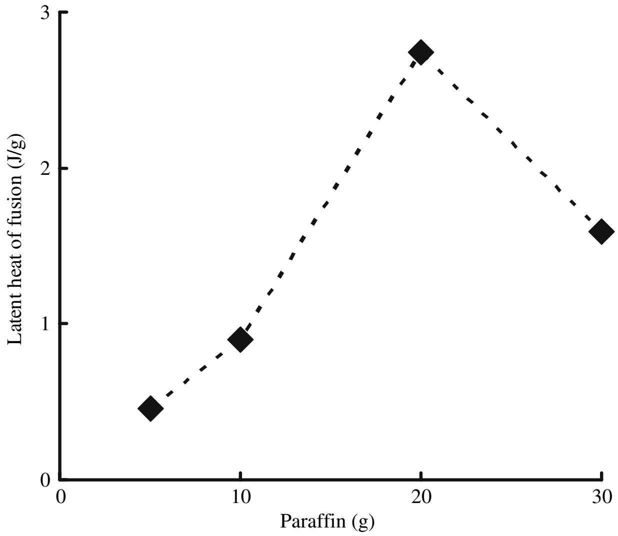


Fig. 7 Effect of the amount of paraffin on the latent heat of fusion, experimental conditions: paraffin, 5–30 g; reaction time, 720 min

added to sample 3 and the reaction time for the interfacial polymerisation between ED and TC on the latent heat of fusion were studied.

Figure 7 shows the latent heat of sample 3, which was prepared using 5, 10, 20 or 30 g paraffin. These values increased as the amount of paraffin added to sample 3 increased and had a maximum with the addition of 20 g paraffin. In the case of 30 g paraffin, the latent heat of fusion decreased. The excess paraffin encapsulated, which could not fix on the paper surface, from the paper surface was thought to leak. The amount of paraffin addition is therefore a preparation condition for sample 3.

Figure 8 represents the latent heat of fusion of sample 3, which was prepared with 1, 5, 10 and 720 min reaction times. The reaction time was defined as the time for the immersion in a cyclohexane solution of TC as outlined in the experimental section “Preparation of sample 3”. The thickness of the nylon film prepared with 1, 5, 10 and 720 min reaction times was the same value and was about 75 μm. This result indicated that the mass percentage of

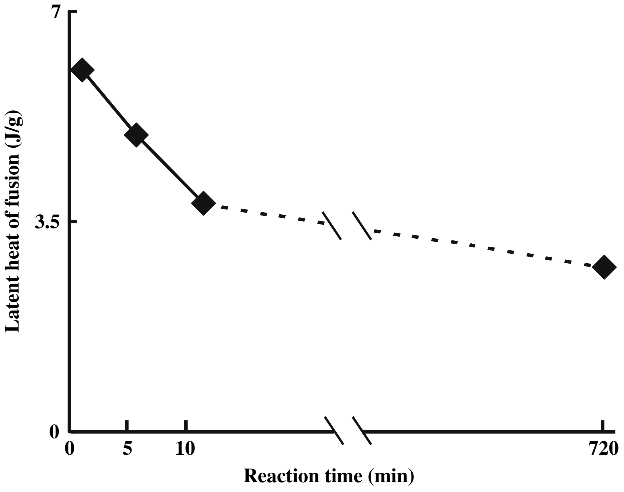


Fig. 8 Effect of the reaction time on the latent heat of fusion, experimental conditions: paraffin, 20 g; reaction time, 1–720 min

nylon film did not increase at the same time. While, the latent heat of fusion of sample 3 tended to decrease as the reaction time increased. Okahata and coworkers reported that nylon film prepared from ethylenediamine and terephthaloyl chloride had a porous structure [15]. Therefore, the paraffin adsorbed on the filter paper was thought to be released gradually to the outer cyclohexane phase as the reaction time increased. The reaction time was also a condition in the preparation of the paper–paraffin composite.

Conclusions

Functional paper containing paraffin as the PCM, which was prepared by interfacial polymerisation on the paper surface after the encapsulation of the paraffin by PMMA, had a thermal energy storage function. When the interfacial polymerisation reaction on the paper surface without encapsulation of the paraffin was carried out, the paraffin leaked from the paper surface. These results suggest that the encapsulation of paraffin was effective in fixing the paraffin with hydrophobicity on the paper with hydrophilicity. This technique would be expected to be a useful in the preparation of functional paper with thermal energy storage without requiring the use of a binder.

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