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Preparation of poly(l-lactide) microcapsules for fragrant fiber and their characteristics

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Abstract

Poly(l-lactide) microcapsules containing fragrant aqueous solution were prepared by interfacial precipitation method through solvent evaporation from (w/o)/w emulsion. The effects of four determinative process parameters on the particle size distributions, surface morphologies, and release behavior of the microcapsules coated with poly(l-lactides) were investigated. As a result, the poly(l-lactide) microcapsules with a narrower distributive, rounder, and more permeable membranes were prepared with the increase of the concentration of protective colloid, solution amount and stirring time. This was related with the surface roughness of the microcapsules. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(l-lactide) microcapsules; Interfacial precipitation; Fragrant fiber

1. Introduction

Currently, much attention is focused on environmental problems and the research and development of biodegradable plastics as high functional materials have been done by many researchers [1–5]. Poly(l-lactides) which are aliphatic polyesters obtained from lactic acids by the fermentation of glucose or sucrose have been used as resorbent materials in medical practice [6–10].

However, poly(l-lactides) have rarely been studied as microcapsules in industrial parts as well as medical ones, due to their high transition temperature, unlike poly(d- or dl-lactides) with higher degradable properties [11,12]. Moreover, process conditions in the preparation of poly(l-lactide) microcapsules have not been established to prepare biodegradable microcapsules containing functional core materials such as drugs, fragrances, pesticides, dye-stuffs, unlike other synthetic polymers [13,14].

In this study, poly(l-lactide) microcapsules containing Forest-shower fragrance as a core material were prepared and the effects of the concentration of protective colloid, solution amount and stirring time on the particle size distribution, surface morphologies and release behavior of the microcapsules were investigated.

2. Methods

2.1. Microcapsule preparation

Poly(l-lactide) (PLLA, $M_w = 8.0 \times 10^5$) obtained from Shimazu, Japan was used as a wall-forming material. Span 80 as an emulsifying agent, poly(vinyl alcohol) (PVA, $M_w = 1500$, Yakuri Pure Chemicals, Osaka Japan) as a protective colloid, Forest-shower fragrant liquid ($M_w = 227.5$, Seil Perfume, Korea) as a core material, sodium tartrate dihydrate ($M_w = 230$, Junsei Chemical, Japan) as a penetrator, and dichloromethane (Merck) as a solvent were purchased as a reagent grade and used without any further purification.

A 50 ml aqueous solution containing 10 wt% of Forest-shower fragrance as core material and 10 wt% of sodium tartrate dihydrate as a penetrator was prepared. A w/o emulsion was formed by adding the resultant aqueous solution into 200 ml of dichloromethane with 2 wt% of PLLA, and 1.0 wt% of Span 80 as an emulsifying agent under a vigorous stirring rate of 3500 rpm. Subsequently, each 200 ml portion of an aqueous solution with 2 wt% PVA as a protective colloid was added into the resultant w/o emulsion in two steps. The stirring time after adding the first 200 ml of PVA solution was set to 30 min, and then the second 200 ml of PVA solution was added. At the same time, the (w/o)/w solution was heated to about 40°C corresponding to the boiling point of solvent at the rate of 2°C/min.

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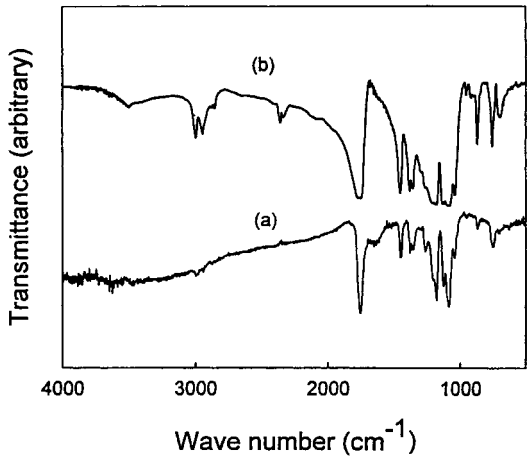

Fig. 1. FT-IR spectra of: (a) poly(l-lactide); and (b) poly(l-lactide) microcapsules with Forest-shower fragrance.

Dichloromethane as a solvent was evaporated thoroughly from the surfaces of w/o emulsion globules for more 2 h to make the interfacial precipitation of PLLA onto the surfaces of the aqueous core materials. The obtained PLLA microcapsules containing the aqueous solutions of a core material and a penetrator were washed with distilled water, filtered, and dried in a vacuum oven at 40°C for at least 12 h.

2.2. Characterization and release test

IR spectra of all the samples were measured using a Nicolet Impact 400D Fourier transform-IR (FT-IR) spectrophotometer. Mean particle size and size distribution of the microcapsules were determined using an Image analyzer Galai CIS-100 (Galai Production Ltd, Israel). The test with few drops of microcapsule slurry was carried out after sonication for 3 min. Scanning electron microscopy (SEM) was performed using a JSM-5400 (JEOL, Japan). Microcapsules were sprinkled onto a double-sided tape, sputter-coated with gold and examined in the microscope. The diagrams from a differential thermal analysis (DTA) and a thermogravimetry (TG) were obtained utilizing TG/DTA30 (SEIKO Electron, Japan). The samples of each about 40 mg were heated to 400°C at the rate of 10°C/min under constant N_2 flow.

A 2 g microcapsule containing sodium tartrate dihydrate as a penetrator and Forest-shower fragrance as a core material was placed in 100 ml of distilled water, stirred mildly and kept at 20°C to obtain the release profile of a penetrator with the same molecular weight as a core material. The concentration of a penetrator released in accordance with stirring time was assayed with a conductive meter (4020 Conductivity meter, JENWAY, USA).

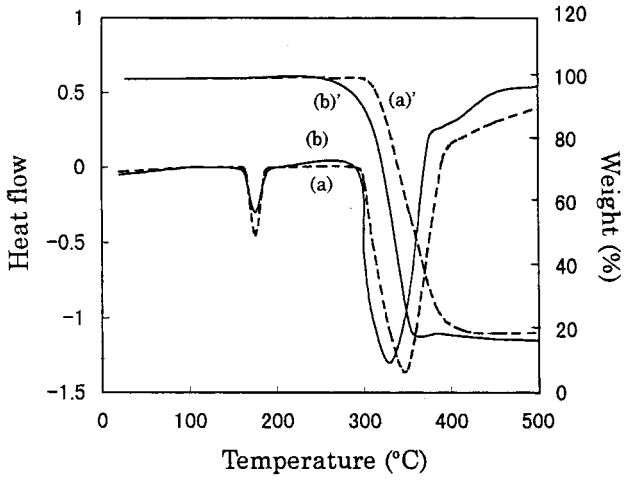

Fig. 2. DTA and TG diagrams of poly(l-lactide) alone ((a),(a′)) and poly(l-lactide) microcapsules with Forest-shower fragrance ((b),(b′)).

2.3. Preparation of fragrant functional fabric

A printing paste was prepared by mixing 5 g of acrylic binder (Binder S, Taepyungyang Chemicals, Korea), 10 g of fragrant microcapsules, 5% OWF (weight percent of dye to fabric) of reactive dyes(1,4-Diamino anthraquinone, Fluka), 5 ml of volatile oil, and 5 ml of distilled water at room temperature. Then a cotton fabric (1.0 m × 1.0 m, Taekwang Industrial Ltd, Korea) was treated with the printing paste, and dried at 40°C at least for 12 h. The washing durability of a fragrant cotton fabric was investigated up to 15 times in accordance with the laundry test of KSK 0403. The surface morphology of the fragrant fabric after the laundry test was observed by SEM to determine its washing durability.

3. Results and discussion

3.1. Structure of microcapsules

Fig. 1 shows the FT-IR spectra of PLLA alone, and PLLA microcapsules containing the aqueous solution of Forest-shower fragrance and sodium tartrate dihydrate. As shown in Fig. 1(a) and (b), adsorption peaks at 2950–2900, 1750 and 1375 cm^{-1} are assigned to an aliphatic C–H stretching vibration, –C=O of ester, and C–CH_3, respectively. The strong peak of 2950–2900 cm^{-1} in (b) is assigned to the sum of C–H stretchings in PLLA, Forest-shower fragrance, and sodium tartarate dihydrate. The peaks at 3300 cm^{-1} in the both samples are assigned to O–H of PLLA, but the peak intensity at O–H in PLLA microcapsules is stronger than that in PLLA alone. This is due to the encapsulation of a quantity of an aqueous solution with a core material and a penetrator in the PLLA wall.

3.2. Thermal properties

Fig. 2 shows the TG and DTA diagrams of PLLA alone and PLLA microcapsules containing core materials to investigate their thermal properties. As shown in the results of DTA (Fig. 2(a) and (b)), the melting temperature of

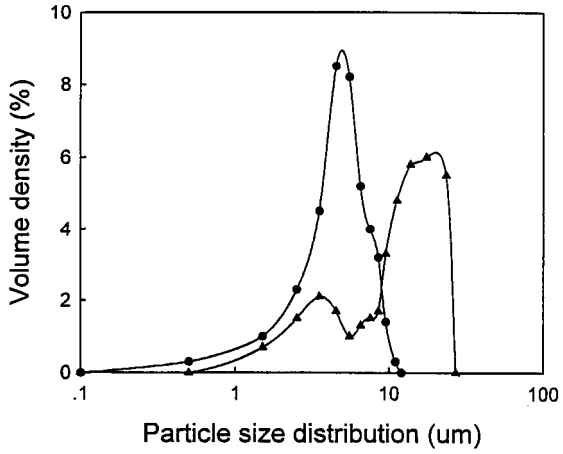

Fig. 3. Particle size distribution of poly(l-lactide) microcapsules at different concentrations of protective colloid: 1 wt% PVA (▲); and 2 wt% PVA (●).

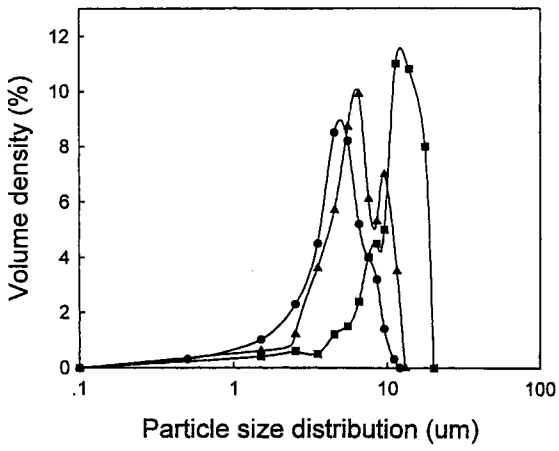

Fig. 5. Particle size distribution of poly(l-lactide) microcapsules at different steps of stirring time: 5–70 min (▲); 15–60 min (●); and 30–45 min (■).

PLLA alone is approximately 175°C and the peak is clearly sharp because of its high crystallinity. However, the absorption peak of PLLA microcapsule containing aqueous solution is smaller, even though the melting temperature hardly changes. In the results of TG (Fig. 2(a)′ and (b)′), any weight loss at melting point is not shown in both PLLA alone and PLLA microcapsules. This can explain that interior aqueous solution was not evaporated due to an agglomerate formation by surface melting among particles. However, the weight of PLLA alone decreases quickly from 310 to 410°C, while the weight of PLLA microcapsules decreases from 260 to 365°C. This can explain that the weight loss of PLLA microcapsules proceeds more rapidly than that of pure polymer due to a plasticization effect of core materials.

3.3. Particle size distribution

Rafati et al. [15] reported that under the conditions of low stabilizer concentration, multi-nucleate particles were formed by polymer precipitation and envelopment of the droplets of the primary w/o emulsion. Also they showed a mechanism for protein microencapsulation, which was heavily influenced by the shear stress induced during the process of secondary emulsification.

In this study, the effects of PVA added to the second emulsion on the size distribution of the microcapsules were investigated. Fig. 3 presents the particle size distribution of

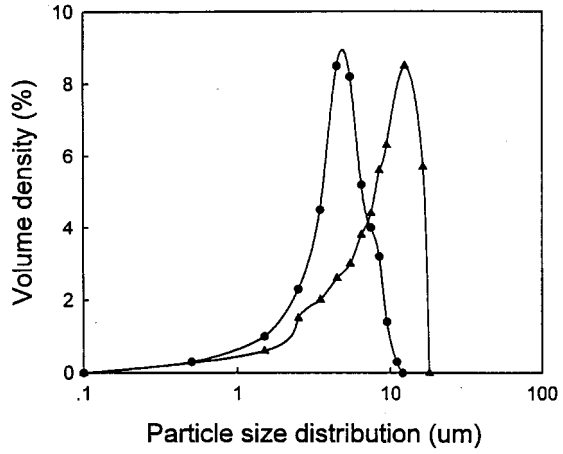

Fig. 4. Particle size distribution of poly(l-lactide) microcapsules at different amounts of protective colloid solution: 200–200 ml (●); and 200–100 ml (▲).

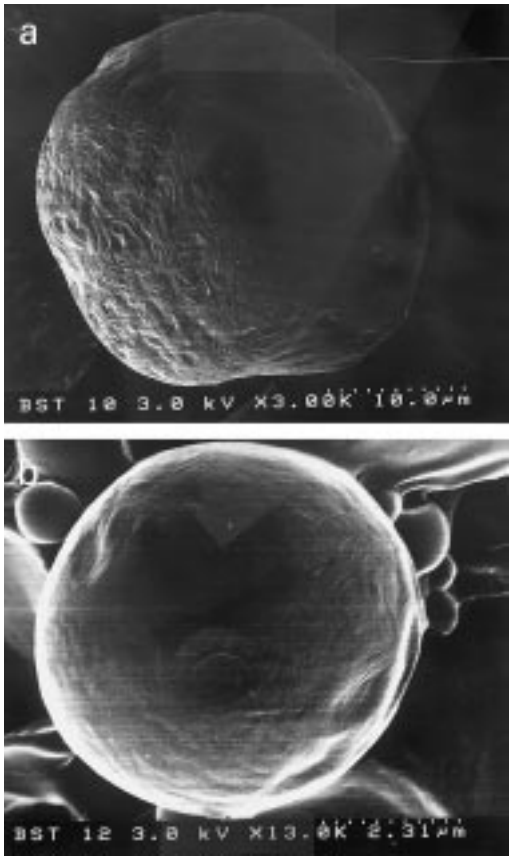

Fig. 6. SEM photographs of poly(l-lactide) microcapsules at different concentrations of protective colloid: (a) 1 wt% PVA; and (b) 2 wt% PVA.

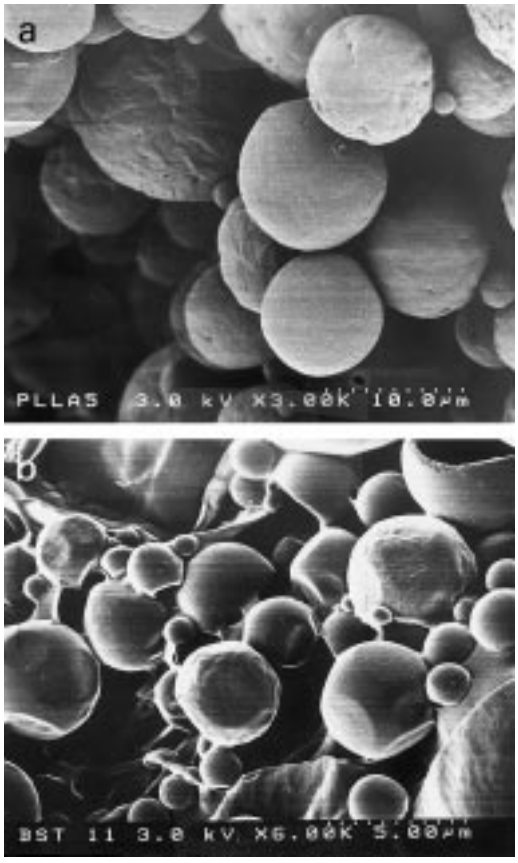

Fig. 7. SEM photographs of poly(l-lactide) microcapsules at different amounts of protective colloid solution: (a) 200–100 ml; and (b) 200–200 ml.

the microcapsules with different concentrations of protective colloid. Mean sizes of the microcapsules for 1 and 2 wt% of PVA were 13.0 and 5.2 μm, respectively. Also the size distribution was narrower with the increase in the PVA concentration, although the globule sizes in w/o emulsion should be the same in general. This seems to be due to a multi-nucleate particle formation with insufficient prevention against coalescence between unstable emulsion globules by adding a smaller quantity of PVA.

Fig. 4 shows the particle size distribution of the PLLA microcapsules at different amounts of the protective colloid solution added to the w/o emulsion in two steps. The particle size distribution of the prepared samples was broader and their mean size also was larger, as the solution volume added to the second step increased from 100 to 200 ml. The amount of the aqueous solution of protective colloid determined the mean diameter of the resulting microcapsules, although the emulsion size should have been the same because the amount of protective colloid added first had been the same. This is related with a collision number among the produced globules in the protective colloid solution. Thus, in the smaller amount of the solution, the particles might be agglomerated by more frequent collision among the unstable emulsion globules.

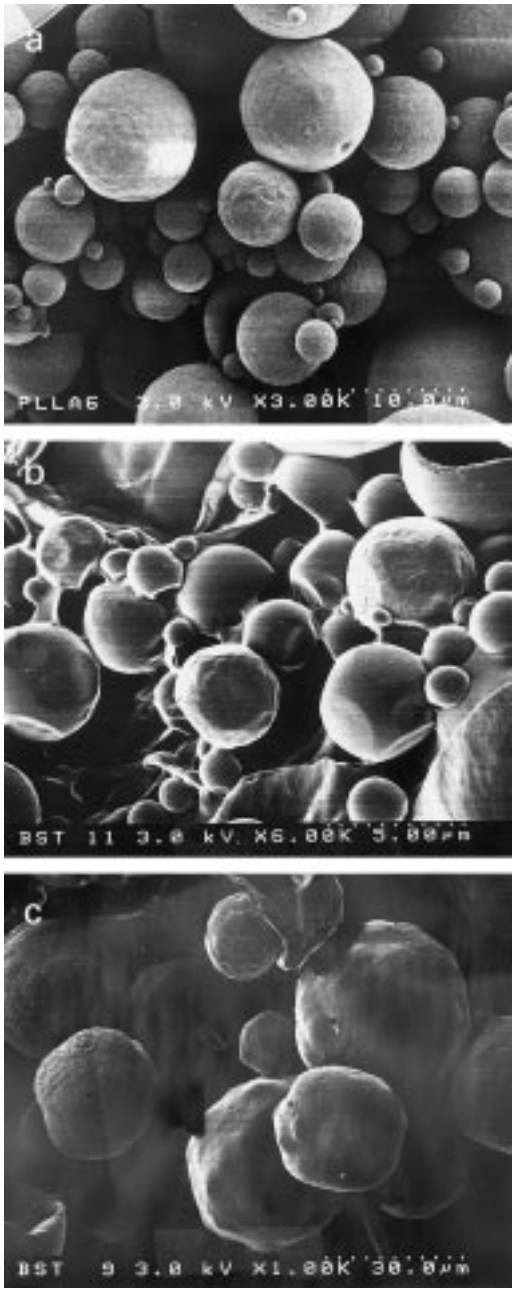

Fig. 8. SEM photographs of poly(l-lactide) microcapsules at different steps of stirring time: (a) 5–70 min; (b) 15–60 min; and (c) 30–45 min.

Fig. 5 shows the particle size distribution of the microcapsules at different steps of stirring time, after adding each 200 ml of the first and the second solutions of protective colloid by setting to 5–70 min, 15–60 min and 30–45 min, respectively. As a result, the mean size of the samples was 6.3, 5.2 and 11.4 μm, respectively. For the latter's, the mean size of the microcapsules was larger with increase in the stirring time in the first stirring. It would allow collision number among the emulsion globules in the constant amount of the solution to increase in accordance with stirring time, and to result in coalescence among the particles.

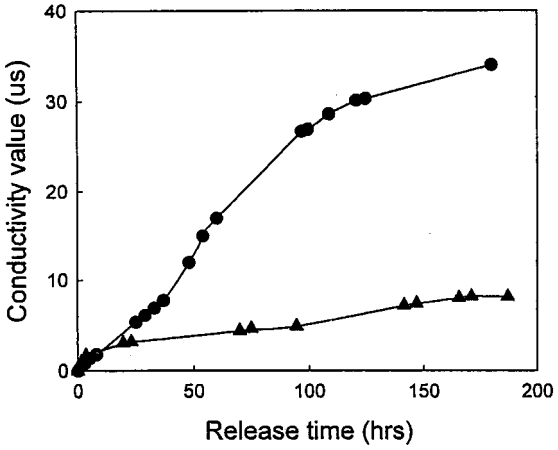

Fig. 9. Conductivity value of sodium tartrate dihydrate from poly(l-lactide) microcapsules at different concentrations of protective colloid: 1 wt% PVA (▲); and 2 wt% PVA (●).

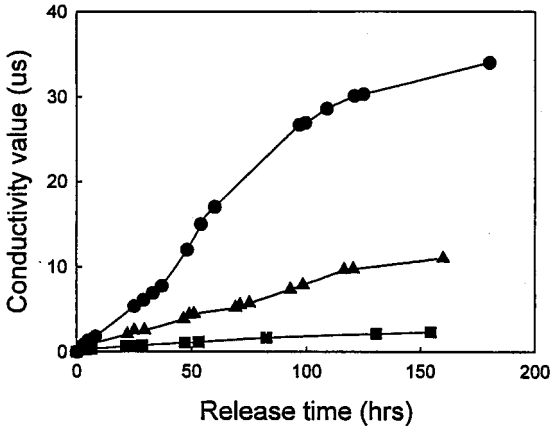

Fig. 11. Conductivity value of sodium tartrate dihydrate from poly(l-lactide) microcapsules at different steps of stirring time: 5–70 min (▲); 15–60 min (●); and 30–45 min (■).

3.4. Morphologies

The surface morphologies of the PLLA microcapsules at different concentrations of PVA are shown in Fig. 6. As shown in the pictures, so many cracks are observed in the surfaces of the microcapsules at 1 wt% PVA, compared with those at 2 wt% PVA. The microcapsules at 1 wt% PVA have less round surface. This results from coalescence among the emulsion globules to produce rougher microcapsule walls.

Fig. 7 shows the morphologies of the microcapsules at different amounts of protective colloid solution. As a result, the surface of the microcapsules in smaller amount in the second addition is rougher, compared with those in larger amount. This can explain that coalescence among particles is due to the insufficiency of the protective colloid solution to allow the microcapsule wall to be rougher.

Fig. 8 presents the surface morphologies of the microcapsules at different steps of stirring time, after adding the first and the second solutions of protective colloid is fixed to 5–70 min, 15–60 min, and 30–45 min, respectively. The stirring time of 15–60 min resulted in the most uniform particles, however those of 5–70 min and 30–45 min made less uniform particles. Insufficient stirring time in the first solution seems to be responsible for a coalescence among unstable emulsion globules, and excessive stirring time in constant content of the first medium also resulted in the coalescence among the globules due to the increase in the collision number in the first medium. Therefore, it is convinced that the adequate combination of medium content and stirring time plays an important part in producing microcapsules in the more uniform size distribution and smoother morphologies.

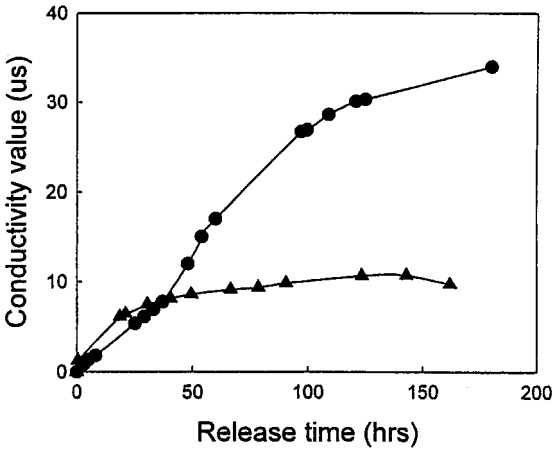

Fig. 10. Conductivity value of sodium tartrate dihydrate from poly(l-lactide) microcapsules at different amounts of protective colloid solution: 200–200 ml (●); and 200–100 ml (▲).

3.5. Release behavior

Rafati et al. showed that almost 80 wt% of the BSA load was released from the sub-micron microparticles produced using 10 wt% PVA stabilizer solution in 25 days, while a low rate of protein release occurred from microcapsules prepared using 1 wt% PVA, amounting to 40 wt% of the protein loading. They suggested this behavior could be related to the larger fraction of protein entrapped within the microparticle core [15]. Fig. 9 shows the release behavior of sodium tartrate dihydrate as a penetrator with the same molecular weight of internal fragrance from the microcapsules prepared at the different concentrations of PVA. As expected in results of size analysis and morphologies, its release rate from the microcapsules at 1 wt% PVA was slower than that from the microcapsules at 2 wt% PVA. This presents the effect of wall roughness, and so the release rate of a penetrator from the wall became slower with the increase in the surface roughness. The surface roughness will enhance the release rate in general due to a large surface area if the microcapsules are multi-nuclear. However, in the

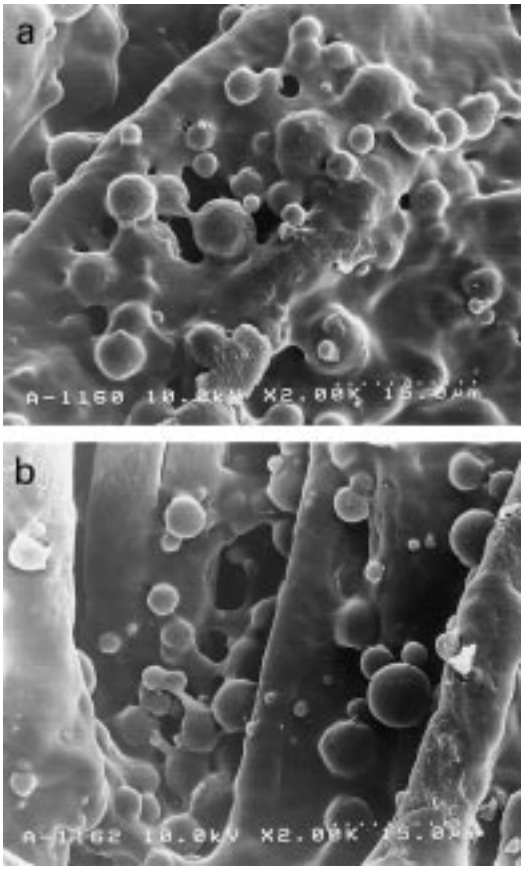

Fig. 12. SEM photographs of cotton fabrics treated with poly(l-lactides) microcapsules after laundry tests: (a) original; and (b) 15 times.

present study, the release rate of the poly(l-lactide) microcapsules with rough surface morphology was slower than those with a smoother one. This indicates that agglomerate among globules had occurred before polymer precipitation onto emulsion globules by decrease of PVA concentration. Therefore, microcapsules with significantly larger mononuclear seem to be prepared unlike microcapsules with multi-nuclear prepared by Rafati et al. [15].

The release behavior of a penetrator from the microcapsules at different amounts of protective colloid solution is shown in Fig. 10. The release rate from the capsule membranes became much slower with the decrease in the medium content. Thus the membranes from the smaller medium amount of protective colloid were almost less permeable due to the coalescence among the particles.

Fig. 11 shows the release behavior of sodium tartrate dihydrate as a penetrator from the microcapsules at different steps of stirring time. The release rate was down to 15–60 min, 5–70 min, and 30–45 min and the permeable rate of the microcapsule wall prepared at 30–45 min was the slowest in accordance with the result in Fig. 7. This can explain that the use of stirring time results in the wall membranes with different release rate.

3.6. Preparation of fragrant functional fabric

Fragrant functional fabrics were prepared by the printing treatment of microcapsules on cotton fabric, and SEM photographs after laundry tests of original and 15 times are shown in Fig. 12. As shown in the pictures, the fabric is coated uniformly by printing paste with microcapsules, and has almost uniform particles on it. Moreover, it is convinced that the particles below 10 μm are applicable for the preparation of functional fabric. Most of the particles, especially much finer ones with mean diameter below 5 μm remain even after the laundry test of 15 times. Thus, fragrant fabric with washing durability was successfully prepared.

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