THE INFLUENCE OF CORE – SHELL RATIO ON CHARACTERISTICS OF MICROCAPSULES CONTAINING CINNAMON ESSENTIAL OIL APPLIED TO AROMATHERAPEUTIC TEXTILES

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Abstract: *Microencapsulation is one of the techniques to prepare the functional textiles. In this paper the essential cinnamon oil loaded microcapsules were prepared by solvent evaporation method. In the microencapsulation process, the core - shell ratio was changed by altering the cinnamon oil content in four levels of 0.15, 0.25, 0.35 and 0.45 g while the other components remained unchanged. The microcapsule characteristics including shape and morphology, size and size distribution, microencapsulation efficiency in dependence on the core-shell ratio were investigated. The antimicrobial capacity and the fragrance durability of interlock knitted fabric coated with the elaborated microcapsules were evaluated. The results showed that cinnamon oil was microencapsulated successfully in the spherical microcapsules. When the cinnamon oil content increased, the microcapsule size decreased and the size distribution became broader, the microcapsules were more porous and more aggregate, the fragrance intensity of the fabric treated with microcapsules increased while the activity against E. coli bacteria decreased. According to the results, the microcapsules elaborated with 0.15 g of cinnamon oil was recommended for the treatment of interlock cotton knitted fabric to apply in aroma and antimicrobial textiles.*

Keywords: *Microencapsulation, solvent evaporation technique, fragrance textile, antimicrobial textile, healthcare textile, interlock knitted fabric.*

1 INTRODUCTION

Today the development of technologies and the rise in environment protection demand orient to the innovation of many new, cleaner, and greener techniques in textile processing. That leads to find the application of microencapsulation in many textile fields such as phase-change materials, fragrance finishes, fire retardants, polychromic and thermo-chromic microcapsules (color - changing technology), antimicrobials, counterfeiting… [1]. The microencapsulation has become a prominently effective technique which enhances the property imparted to the fabric and assures its durability. Microencapsulation is a technique to prepare the tiny particles that contain an active agent in a core and a polymer material surrounded or shell that can limited the liberation of active agent. Microcapsules help to control release of active compounds (sustained, delayed, or targeted release). Besides, they also help to increase the stability of the active agent against oxidation or deactivation by the environment. Other advantages are masking odor, taste, and some side effects of active agents.

Fragrant textile products using the microencapsulation techniques were the subjects of many researches [2-4]. Especially, using microcapsules containing essential oil extracts for healthcare textiles such as antimicrobial and aroma therapeutic ones has been in concern of many studies [2-8].

The satin weave cotton fabrics have been coated with microcapsules containing oil extracted directly from neem leaves and Mexican daisy [5]. The microcapsules were made by simple coacervation method using the oil herbal extracts as active core material and gum acacia as wall material. The antibacterial test was conducted against the *Staphylococcus aureus* and *Escherichia coli*. In case of fabric direct treatment with oil herbal extracts, the antimicrobial efficacy was 100 % and 78.44 % against *Staphylococcus aureus* and *Escherichia coli* respectively. That values for the fabric treated with oil herbal extracts by microcapsules were 93.45 % and 55.21 %. However, the antimicrobial durability test showed the advantage of microcapsules in keeping the antimicrobial efficacy after washing compared to the direct treatment. In case of using neem extract, the bacterial reduction percentage after 15 washing cycles of fabric treated with microcapsules was 78 % and of the fabric directly treated with extract was 41%. For Mexican daisy extract, these values were 67 % and 37 % respectively. Especially, the direct treatment of fabric with oil herbal extracts but

without cross linking agent led to the bacterial reduction percentage of 0 % after 15 washing cycles.

Karagönlü S. et al. elaborated the thyme oil loaded microcapsules for antimicrobial textile [6]. The microcapsules were made by complex coacervation method using thyme oil as active agent, gelatin and gum arabic as wall materials. The effect of microencapsulation parameters such as amount of oil and concentration of wall material on the encapsulation yield, particle size distribution and oil loading were investigated. It was reported that microencapsulation yield increased as the amount of oil increased, but the microcapsule shape became more irregular. Moreover, when the amount of wall material in solution increased, the formation of capsules diminished. The antimicrobial capacity of microcapsules and fabrics coated with microcapsules were determined. Antimicrobial activity test demonstrated that both microcapsules and fabrics treated with different microcapsule concentrations showed antimicrobial activity against E. coli, S. aureus and C. albicans microorganisms.

Many papers presented the aroma textile fabrics treated with microcapsules containing natural essential oil which prepared by coacervation and polymerization in situ [7-8]. The durable aroma finish on cotton fabric using microencapsulation technology was conducted by Bhatt L. [7]. In the research, the microcapsule gel was prepared by simple coacervation technique using four kinds of natural essential oil (basil oil, lemongrass oil, orange oil, tea tree oil) as core materials and the gelatin and gum acacia were the membrane of microcapsules. The most efficacy essential oil was considered as lemongrass oil and the research had used it for further works. Cotton fabric was padded with microcapsule gel containing lemongrass oil, the curing temperature and time were optimized at 80°C for 60 seconds. Then the washing durability of fragrance was evaluated by 20 experts through a survey technique using olfactory analysis. According to the research, fabric samples retained aroma for up to 30 wash cycles and the aroma intensity decreased when the number of wash cycles increased. Percentage of fragrance remaining on fabric before washing and after 5, 10, 15, 20, 25, 30 wash cycles were reported as 100 %, 100 %, 100 %, 95 %, 85 %, 75 % and 20 % corresponding. Microencapsulation of fragrance and natural volatile oils for application in cosmetic textile was studied by Tekin R. et al. [8]. The microcapsules with diameters ranging from 10 mm to 80 mm were prepared by interfacial polymerization technique using the fragrance Teddysoft as core material, PVA as surfactant and the polymer wall of microcapsules was the polyurethane. The hand towels were treated with fragrance by two techniques that were microcapsule coating and mixing the fragrance in fabric softener base. These hand towels passed the laundering cycles and were kept for a week to qualitatively evaluate the fragrance by nine perfumers and by headspace-GCMS analysis. Both the evaluations by the perfumers and by headspace-GC analysis showed that the hand towels washed with the fabric softener including more microcapsules smelt stronger after a week and more volatile compounds of the fragrance existed on the hand towels when the fragrance was encapsulated. The results demonstrated the efficacy of microencapsulation technique to maintain the fragrance for textile products.

The method to evaluate qualitatively and quantitatively the fragrance of textile products was mentioned in many researches [8], [9]. The team of experts was considered the best method because of the limitation of electronic devices to a great number of odorants. Stan M. S. et al. developed the textile materials for cosmetic purposes by applying sage melamine microcapsules containing essential oil to woven fabrics from different fiber compositions (100% cotton and 50% cotton/50% polyester) [10]. The authors investigated the influence of the overall finishing processes on the physical-mechanical characteristics such as mass per unit area, maximum force, elongation at maximum force, water vapor permeability and permeability to air. The small and normal influence on fabric physical-mechanical characteristics of the microcapsule treatment by pad-dry-cure method was shown. The test of biological properties indicated good biocompatibility and helped to conclude that the fabric treated by essential oils loaded microcapsules could be used for the cosmetotextile industry, providing certain biological properties, such as antioxidant, anti-inflammatory, antibacterial and flavoring effect.

Microencapsulation by situ polymerization was used for many different textile applications: antimicrobial essential oils of sage, lavender and rosemary for nonwoven textile shoe insoles; smell-based animal repellents for agricultural textiles, textiles for plant protection against damage caused by deer and rabbits; and paraffinic phase change materials (PCMs) for active thermal control garments [11]. In these cases, melamine formaldehyde prepolymer was often used as wall materials. In microencapsulation process, the technical parameters were manipulated to obtain desired characteristics of microcapsules: the microcapsule wall had to be partially permeable in the case of animal repellents in order to slowly release the essential oil in the microcapsule core by diffusion/evaporation and to achieve a prolonged release; but the microcapsule wall had to be impermeable and pressure-sensitive to achieve a targeted release during walking and no release when the shoes were not worn in the case of textile shoe insoles. Moreover, the mechanical resistance of microcapsule wall needed to assure a sufficient mechanical strength to withstand solid-liquid transitions of PCMs microcapsule core without leaking.

Beside the coacervation and polymerization techniques, the solvent evaporation method is used widely to elaborate microcapsules for many textile applications such as cosmetic and fragrant textile, medical textile, thermoregulating textile, antimicrobial and antifungal textile… [12]. Simple process and equipment as well as no use of toxic monomers are the main advantages of solvent evaporation method in comparison to coacervation and polymerization techniques. In the microencapsulation by solvent evaporation method, the mass ratio of active ingredient to polymer was reported to have marked effects on microcapsule morphology, especially the structure of the shell [13 -16]. In the research of Merabedini S. M. et al. [14], the plant oils were encapsulated in ethyl cellulose microcapsules by solvent evaporation method. The mass ratio of active ingredient to polymer varied in three levels of 60:40, 70:30, and 75:25. The results showed that the increase of core - shell ratio made the polymer shell more porous with much tinier holes on the surface. According to the authors, too much of active ingredient might increase the risk of active ingredient leakage due to the limited space inside the microcapsule and the shrinkage of the microcapsule during its solidification, resulting in the more porous polymer shell with an increasing number of holes.

This work aimed to study the ability of microencapsulating cinnamon essential oil by solvent evaporation method. The effect of core - shell ratio in the microencapsulation process on some microcapsule characteristics such as microcapsule shape and morphology, microcapsule size and size distribution, microencapsulation efficiency were investigated. The change in antimicrobial capacity and the fragrance durability of fabric treated with microcapsules according to the core - shell ratio was also in concern.

2 EXPERIMENTAL METHODS

2.1 Materials

Natural cinnamon oil supplied by Vietessence (Vietnam) was used in combination with miglyol 812 from Sasol as the core ingredients of the microcapsules. The Poly(ethyl acrylate-co-methyl methacrylate-co-trimethylammonioethyl methacrylate chloride) (Eudragit RSPO) of Evonik Industry (Germany) was used as the polymer shell of the microcapsules. The solvent of ethyl acetate with purity of 99.9% was supplied by Merk (Germany). Quillaja saponin S4521 from Sigma Aldrich (Germany) with molecular weight of around 1650 Da and contained 20 ÷ 35% of the sapogenin content was the surfactant. All chemical products have been used as providing without any more purification.

The cotton interlock fabric was knitted from cotton yarn with yarn count of Ne40 on circular knitting machine Fukahara (Japan). The knitting gauge was E18. The grey fabric was then scoured, bleached, and fully relaxed to get the dimensional stability. The fabric at fully relaxed state had the loop length of 2.83 mm, the course density of 188 courses/10cm, the wale density of 152 wales/10cm, and the weight of 240 g/m^2.

2.2 Methods

2.2.1 Microencapsulation

The organic phase was 15 ml of ethyl acetate solution containing cinnamon oil (varied with four levels of 0.15, 0.25, 0.35 and 0.45 g, miglyol 812 (0.4 g) and eudragit RSPO (1.25 g). Miglyol 812 was mixed with cinnamon oil in the microcapsule core to slow down the evaporation of essential oil from the microcapsule. That meant the core - shell ratio was changed in an increasing order of 1/2.3; 1/2; 1/1.7; and 1/1.5.

The organic phase was added dropwise to 100 ml aqueous solution of quillaja saponin (0.075 wt%) at stirring rate of 700 rpm for 10 minutes. At the end of the organic phase addition, the evaporation of ethyl acetate was initiated at reduced pressure (300 ÷ 350 Torr) for 5 hours under stirring at 600 rpm. The microcapsules were collected and washed three times by sedimentation and after that were stored as 100ml of suspension in distilled water in the lab fridge.

The microencapsulation efficiency was defined as the weight percentage ratio of the totally dry microcapsules to corresponding original materials. To determine this value, 20 ml of stored microcapsule suspension in water was sedimented to take out the solid microcapsules. After that, the solid microcapsules were dried in the lab fridge (relative air humidity of 20 % and temperature of 8°C) until the weight remained constants. The microencapsulation efficiency E [%] was calculated by (1):

$$E = \frac{M_{mc}}{M_{raw}} 100. \qquad (1)$$

In which, M_{mc} was the weight of totally dried microcapsules and M_{raw} was the weight of corresponding original materials.

2.2.2 Microcapsule characterization

The microcapsule morphology was observed by the scanning electron microscope (SEM) JEOL JSM-7600F, USA at working conditions of 5.0 kV; LM mode; WD 8.0 mm. For the original microcapsules, a small drop of stored microcapsule suspension was placed on the sample holder of SEM equipment. For the fabric treated with microcapsules, a small piece of fabric was stick to the sample holder with the fabric surface containing microcapsules faced up. The observation was captured at magnifications of x100, x500 for the overview of whole microcapsule lot and at x10,000 for the details on the microcapsule polymer shell.

The mean diameter and the size distribution of microcapsules were determined by static laser - light scattering on Laser Scattering Particle Size Distribution Analyzer LA - 950 of Horiba. The broadness of the size distribution curve is

represented by the span value, which was calculated as below:

$$Span = \frac{d(0.9) - d(0.1)}{d(0.5)} \quad (2)$$

In which *d*(0.9) meant that 90% of the total particles were smaller than this size, the meaning of *d*(0.1) and *d*(0.5) were similar.

2.2.3 Fabric treatment with microcapsules

The circle fabric sample with diameter of 88 mm was placed at the bottom of plastic circle cup with the inner diameter as the same to that of fabric. 20 ml of stored microcapsule suspension in water was diluted with 20 ml of distilled water and then 40 ml of the diluted suspension was poured into the cup. The system was kept in place for the microcapsules to settle on the fabric surface. After 24 hours of sedimentation, the fabric impregnated with microcapsules was gently taken out of the cup and was dried in the lab fridge (relative air humidity of 20 % and temperature of 8°C) until the weight remained constants.

The microcapsule amount loaded by the fabric M [g] was calculated by (3):

$$M = M_2 - M_1 \quad (3)$$

With M_1 and M_2 were the weight in gram of the fabric before and after treatment with microcapsules, respectively.

The microcapsule loading efficiency of fabric MLE [%] was defined as (4) as below:

$$MLE = \frac{M}{M_0} 100\,. \quad (4)$$

In which, *M* was the microcapsule amount loaded by the fabric and M_o was the microcapsule amount used to treat the fabric, both were in gram. Because 20 ml in the whole of 100 ml of stored microcapsule suspension was used in the fabric treatment, M_o was equal to 1/5 of the total mass of the elaborated microcapsule lot.

2.2.4 Fragrance intensity evaluation

The fragrance intensity of fabric samples treated with microcapsules containing the cinnamon essential oil was evaluated by expert method in combination with the comparison to diluted sample method according to a magnitude scale procedure. The aqueous solution of microcapsule was gradually diluted by distilled water and was kept closing tightly in a small bottle of 10 ml. Eleven bottles were prepared with different ratio of microcapsule volume solution, which were 0 %, 10 %, 20 %, 30 %, 40 %, 50 %, 60 %, 70 %, 80 %, 90 % and 100 %, corresponding to the points of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100. The bottle of total distilled water was “no odor” and was considered as “blank”. Five experts were trained to participate in the evaluation of the fragrance. The result was the average value given by the five experts.

2.2.5 Antibacterial activity test

The antibacterial activity of microcapsule treated fabric was tested again E. coli Gram - negative gram bacteria according to the testing standard of FTTS-FA-002. A sample of untreated fabric was used as control sample. The result was represented by E. coli bacteria reduction [%] and each test was duplicated.

3 RESULTS AND DISCUSSIONS

3.1 Influence of core - shell ratio on microcapsule characteristics

The core - shell ratio is an important formulation parameter in the microencapsulation process because it has strong impact on the microcapsule characteristics such as shape and morphology, size distribution, microencapsulation efficiency and release behavior of essential oil from the microcapsules.

To investigate the effect of core - shell ratio on the microcapsule characteristics, the mass of cinnamon oil was changed in four levels, while this of the other components in the microencapsulation formulation remained unchanged. The four levels of cinnamon oil content were 0.15; 0.25; 0.35 and 0.45 g corresponding to the total core - shell ratio of 1/2.3; 1/2; 1/1.7; 1/1.5, respectively (the total core mass was the sum of cinnamon oil mass and miglyol 412 mass in the microencapsulation formulation). The microcapsule shape and morphology, the microcapsule size distribution and the microencapsulation efficiency were determined.

3.1.1 Influence of core - shell ratio on microcapsule shape and morphology

The microcapsule shape and morphology were observed by scanning electron microscope (SEM).

SEM images at Fig. 1 showed spherical microcapsules with size ranging from about 1 to 60 µm, which was reported to be suitable for textile applications [2], [3], [5], [15]–[18].

Some broken microcapsules could be seen in all four microcapsule lots M1 - M4 and they were often at large size of about more than 50 µm. That might be the result of very fast diffusion of ethyl acetate from emulsion droplets with bigger size to the aqueous phase during the emulsification and the evaporation steps. The solubility in water of ethyl acetate (90 g/l at 20 °C) is higher than that of halogenated solvents commonly used in the solvent evaporation method such as dichloromethane (20 g/l at 20 °C), so the fast diffusion rate of ethyl acetate from oil droplets to aqueous phase may disturb the emulsification step and induce the formation of broken microcapsules.

Besides, the microcapsule aggregates were shown clearly in the SEM images of all four microcapsule lots. The aggregates contained many small microcapsules adhering to the surface of bigger ones.

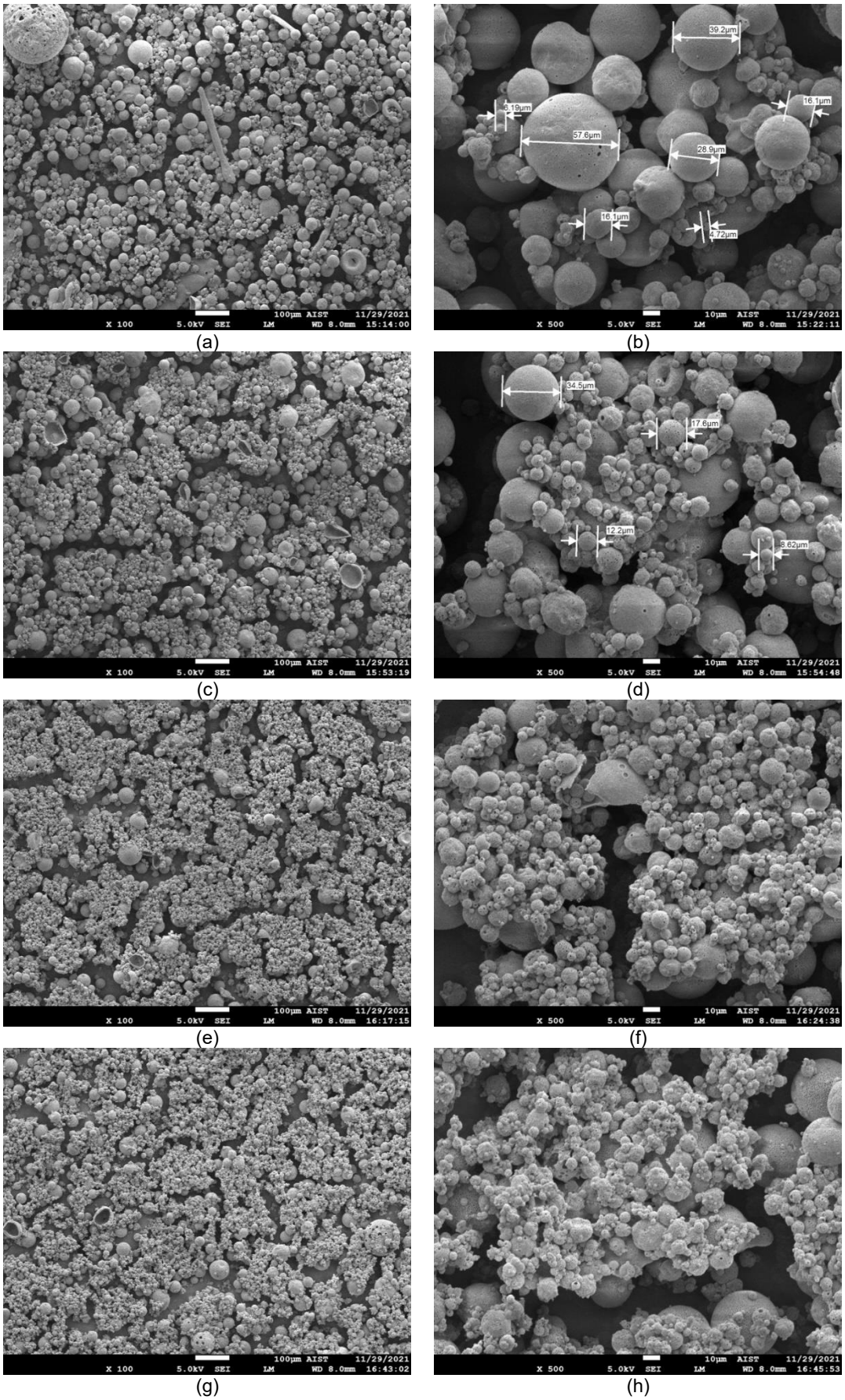
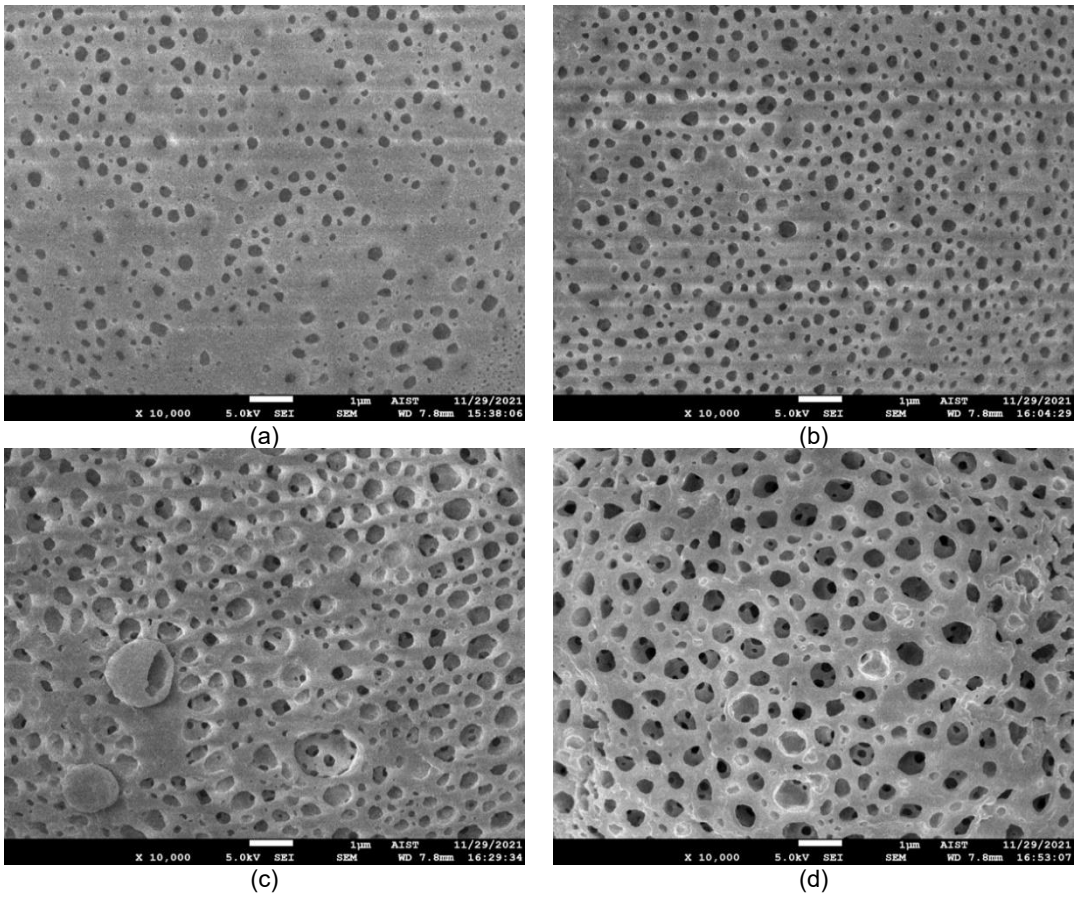


Figure 1 SEM images of microcapsules with (a and b) 0.15 g, (c and d) 0.25 g, (e and f) 0.35 g and (g and h) 0.45 g of cinnamon oil in the microencapsulation formulation



(a) (b) (c) (d)

Figure 2 SEM images of the microcapsule polymer shell with (a) 0.15 g, (b) 0.25 g, (c) 0.35 g and (d) 0.45 g of cinnamon oil in the microencapsulation formulation

The aggregation was mentioned as the main feature of microcapsules elaborated by the solvent evaporation technique using ethyl acetate as volatile solvent [14], [19]. Since water solubility in ethyl acetate was 3.3 wt% at 20 °C, the oil droplets could absorb a considerable amount of water during the microencapsulation processes. Therefore, microcapsules might be soften because of the residual ethyl acetate and water migrating into the microcapsule surface, leading to the aggregation of adjacent microcapsules [19].

The SEM images at Fig. 1 also revealed the decrease in microcapsule size, the more porous microcapsule shell as well as the more deformed microcapsule shape when the cinnamon oil mass in the microencapsulation formulation increased. SEM images at the magnification of x10,000 (Fig. 2) helped to capture the microcapsule shell more detail and then confirmed the more porous polymer shell according to the increase of cinnamon oil mass. The more porous shell of microcapsules with higher amount of core material was also reported in some literatures [14]–[16] and it could be due to the lack of polymer shell to encapsule the high loading of oil. The porous polymer shell played an important role in controlling the release of active ingredient in the microcapsule core because the more porous the polymer shell, the easier and faster release of the essential oil from the microcapsule.

3.1.2 Influence of core - shell ratio on microcapsule size and size distribution

The microcapsule size and size distribution are important characteristics of the microcapsules because they determine the total surface area of microcapsules and therefore affect the release rate of cinnamon oil from the microcapsules.

The results of size and size distribution of microcapsules according to the amount of cinnamon oil were introduced in the Fig. 3 and Table 1.

Table 1 Mean size and span value of microcapsule lots M1 (0.15 g), M2 (0.25 g), M3 (0.35 g) and M4 (0.45 g) of cinnamon oil in the microencapsulation formulation

Lot	Amount of cinnamon oil [g]	Mean diameter [µm]	Span value
M1	0.15	48.69	1.6
M2	0.25	40.25	1.9
M3	0.35	33.52	1.7
M4	0.45	27.37	2.0

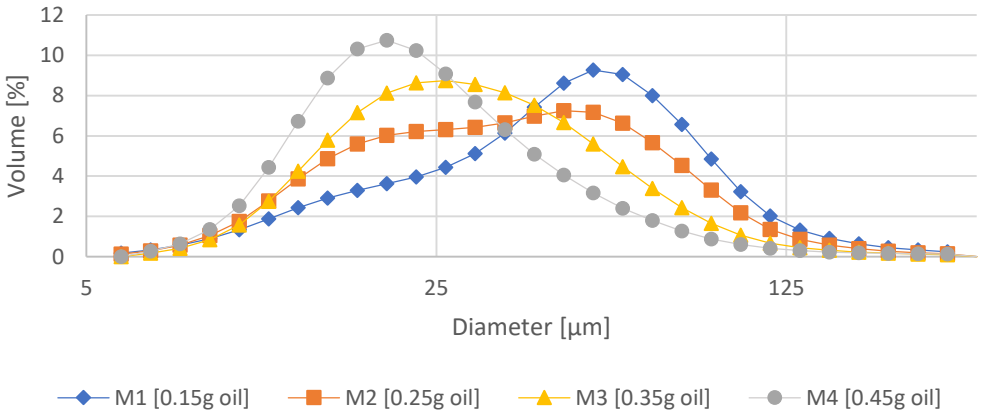


Figure 3 Size distribution of microcapsule lots M1 (0.15 g), M2 (0.25 g), M3 (0.35 g) and M4 (0.45 g) of cinnamon oil in the microencapsulation formulation

The results at Table 1 showed that elaborated microcapsules had the mean diameter of 27 ÷ 48 µm, which confirmed the microcapsule dimension revealed by the SEM images at Fig. 1. The size range of microcapsules containing cinnamon oil in this work was quite popular for textile applications and especially for the fragrant textiles [2], [3], [7], [13], [15], [16].

Moreover, the results at Fig. 3 and Table 1 indicated that when the amount of cinnamon oil increased, the mean size of microcapsules decreased clearly. The mean size of microcapsule lots with the cinnamon oil content of 0.15, 0.25, 0.35 and 0.45 g was 48.69, 40.25, 33.52 and 27.37 µm, respectively. The decrease in microcapsule size according to the increase of cinnamon oil amount also could be seen in the SEM images at Fig. 1. This trend was similar to results reported in another work about the microencapsulation of plant oil using the polymer shell of ethyl cellulose and also by the solvent evaporation technique [14]. The reason for this could be the decrease in the viscosity of dispersed phase when more cinnamon oil was used in the microencapsulation process. Because the rate of stirring blade during the emulsification was not altered (at 700 rpm), it would be easier to disrupt the emulsion droplets into smaller ones when the viscosity of the dispersed phase decreased.

Besides, it was remarkable that the increase of cinnamon oil amount induced the broader size distribution of microcapsules, which was shown by the increase of span value (Table 1) and the size distribution curves at Fig. 3. In general, the span value of four microcapsule lots was in range from 1.6 to 2.0 that was quite high, and the size distribution curves were all in type of bimodal ones as in Fig. 3.

3.1.3 Influence of core - shell ratio on the microencapsulation efficiency

Microencapsulation efficiency is the percentage ratio of the weight of elaborated microcapsules to the total weight of original materials, so it is also an important feature of a microencapsulation process. The microencapsulation efficiency corresponded to different amount of cinnamon oil was presented at Table 2:

Table 2 Microencapsulation efficiency according to the different amount of cinnamon oil in the microencapsulation formulation

Lot	Amount of cinnamon oil [g]	Microencapsulation efficiency [%]
M1	0.15	49.76
M2	0.25	49.15
M3	0.35	43.18
M4	0.45	37.24

The microencapsulation efficiency corresponded to four investigated levels of cinnamon oil content was in range from 37 to 50%. Within the scope of investigation, the microencapsulation efficiency tended to decrease slightly according to the increase in the cinnamon oil content. When cinnamon oil content increased 3 times from 0.15 g to 0.45 g, then the microencapsulation efficiency decreased about 1.4 times from 50% down to 37%. Too much of oil could induce the lack of polymer to make enough strong microcapsule shell, which led to not only the more porous polymer shell as mentioned above (Fig. 1 and 2) but also the lower microencapsulation efficiency.

3.2 Influence of core - shell ratio on the characteristics of the cotton interlock knitted fabric containing microcapsules

As discussed above, the core - shell ratio had effect on the main microcapsule characteristics such as shape and morphology, size, and size distribution. The microcapsule shape and size were important factors that determined the performance of textile containing microcapsules. Therefore, it was necessary to investigate the change in some characteristics of fabric treated with microcapsules when the core - shell ratio altered.

3.2.1 Influence of core - shell ratio on the surface morphology of fabric containing microcapsules

The surface of cotton interlock knitted fabric treated with microcapsules was observed by SEM and the results were shown in Fig 4.

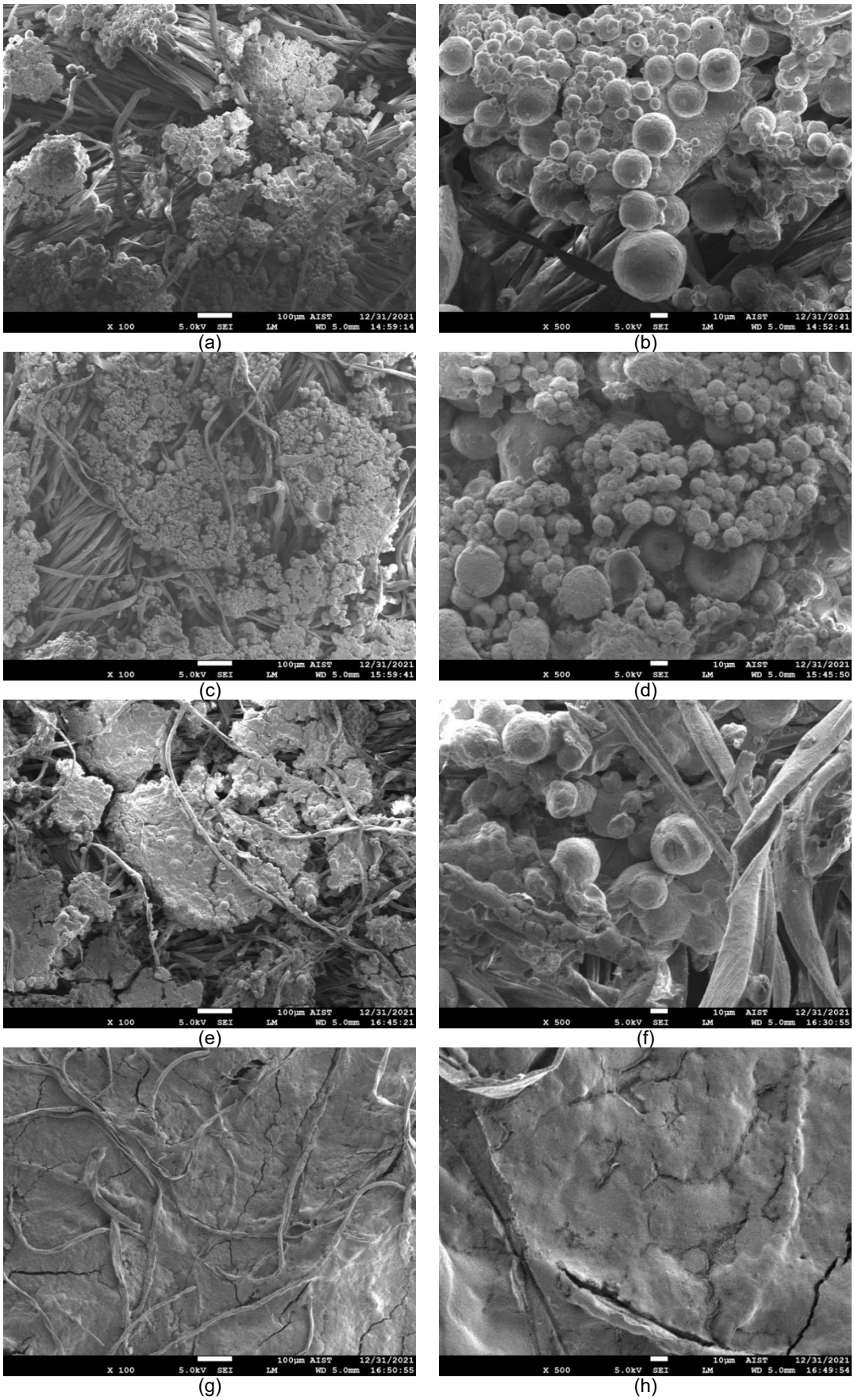
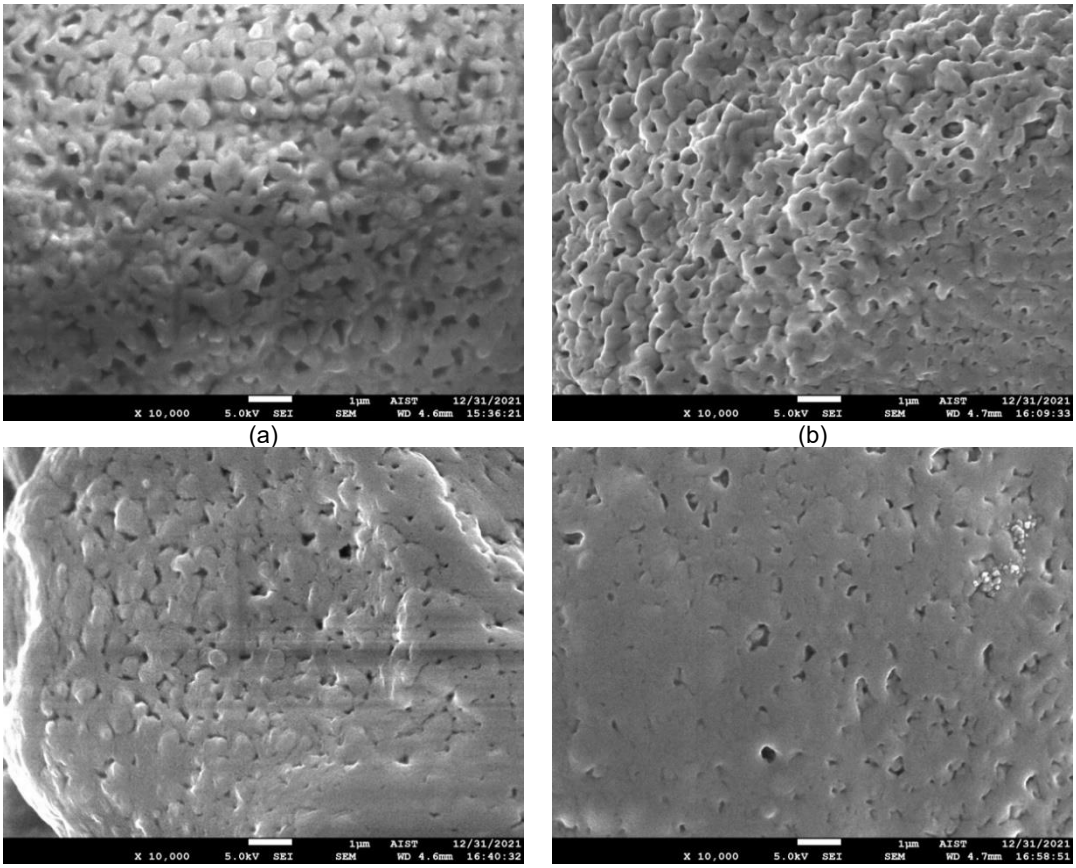


Figure 4 SEM images of cotton interlock fabric treated with microcapsules (a,b) – treated with M1 microcapsules (0.15 g of cinnamon oil); (c,d) – treated with M2 microcapsules (0.25 g of cinnamon oil); (e,f) – treated with M3 microcapsules (0.35 g of cinnamon oil); (g,h) – treated with M4 microcapsules (0.45 g of cinnamon oil)



(a) (b)

(c) (d)

Figure 5 SEM images of the microcapsule polymer shell after the fabric treatment (a) M1 microcapsules (0.15 g of cinnamon oil); (b) M2 microcapsules (0.25 g of cinnamon oil); (c) M3 microcapsules (0.35 g of cinnamon oil); (d) M4 microcapsules (0.45 g of cinnamon oil)

SEM images at Fig. 4 helped to confirm the successful impregnation of microcapsules to the cotton interlock fabric. However, the distribution of microcapsules on the fabric surface was not uniform. Instead, the microcapsules tended to stick together and agglomerate into clumps. Moreover, the microcapsules dried on the cotton fabric surface (Fig. 4) deformed much seriously than being dried in original state (Fig. 1). The fabric surface structure, at the micro scale, was not completely flat but rather bumpy. Besides, as discussed above, the microcapsules elaborated by solvent evaporation technique using ethyl acetate solvent tended to make aggregate by themselves. When the microcapsules were impregnated to the fabric, the bumpy structure of the fabric surface enhanced the ability of the wet microcapsules to stick together and coalesce. During the drying stage, the wet microcapsules that coalesced were dried slower than individual ones, the polymer wall of microcapsules in the coalescence was weaker than that in the individual ones, so they became the deformed aggregate of microcapsules on the fabric surface after drying stage.

SEM images at Fig. 4 also revealed the more serious deformation of microcapsules with more cinnamon oil content in the elaborating formulation. Especially, in the case of M4 lot (with maximum oil content of 0.45 g), the microcapsules on the fabric surface deflated dramatically after the treatment. As described above, higher cinnamon oil amount contributed to the more porous polymer shell of microcapsules, which would be weaker and easier to be deformed during the impregnating and drying stage.

SEM images at Fig. 5 showed the wrinkle microcapsule shell after the fabric treatment with all four investigated microcapsule lots.

That could be the consequence of polymer diffusion during the drying stage in the fabric treatment process. The more oil content of the microcapsules, the weaker of the microcapsule shell, then the more serious diffusion of the polymer as observed by SEM. The diffusion of eudragit RSPO polymer shell also altered the structure of holes on the microcapsule surface. As compared to the SEM images of polymer shell before fabric treatment (Fig. 2), the holes became much smaller. Besides, on the cotton interlock fabric, the polymer shell of microcapsules with higher cinnamon oil content were less porous, which was in contrast with the tendency observed on the microcapsules alone (before the fabric treatment).

3.2.2 Influence of core - shell ratio on the fragrance intensity of fabric containing microcapsules

The cinnamon oil used in the microencapsulation formulation would affect the oil content in the fabric treated with microcapsules and then, would determine the fragrance intensity of the fabric. So, the influence of core - shell ratio on the fragrance intensity of microcapsule treated fabric was studied by varying the cinnamon oil content while the quantity of other materials in the microencapsulation process remained unchanged. The four levels of cinnamon oil content investigated were 0.15, 0.25, 0.35 and 0.45 g, corresponding to the microcapsule lots of M1, M2, M3 and M4.

The fragrance intensity of the fabric treated with microcapsules was determined by expert evaluation after the certain periods of 3, 5, 7, 9, 11, and 13 days. The average evaluation of five experts were represented in the Table 3 and Fig. 6.

As shown in the Table 3 and in the chart at Fig. 6, all four microcapsule lots did help to add the fragrance of cinnamon oil to the cotton interlock fabric. The fragrance intensity in the fabric decreased gradually by times but the odor was still being detected by the experts after 13 days.

It should be noted that the change in cinnamon oil content altered the microencapsulation efficiency. So, with the same volume of stored microcapsule suspension used to treat the fabric (20 ml, equal to 1/5 of the whole microcapsule lot), the microcapsule amount loaded by the fabric would be different. Therefore, the microcapsule amount loaded by the fabric as well as the microcapsule loading efficiency of the fabric were determined and the results was shown in the Table 4.

There was some variance in the microcapsule loading efficiency of fabrics treated with the different microcapsule lot and the dependence of this value on the cinnamon oil content did not follow a clear trend. This will be investigated and discussed more in further research.

Table 3 Fragrance intensity of microcapsule treated fabric after certain periods of time

Microcapsule lot used for fabric treatment	Cinnamon oil content [g] in the microencapsulation formulation	Fragrance intensity					
		After 3 days	After 5 days	After 7 days	After 9 days	After 11 days	After 13 days
M1	0.15	12.0	10.3	9.0	8.0	4.3	3.3
M2	0.25	17.0	11.1	8.8	6.3	3.1	1.8
M3	0.35	21.8	12.2	10.7	9.1	4.8	3.9
M4	0.45	26.3	15.8	13.3	11.3	6.3	4.0

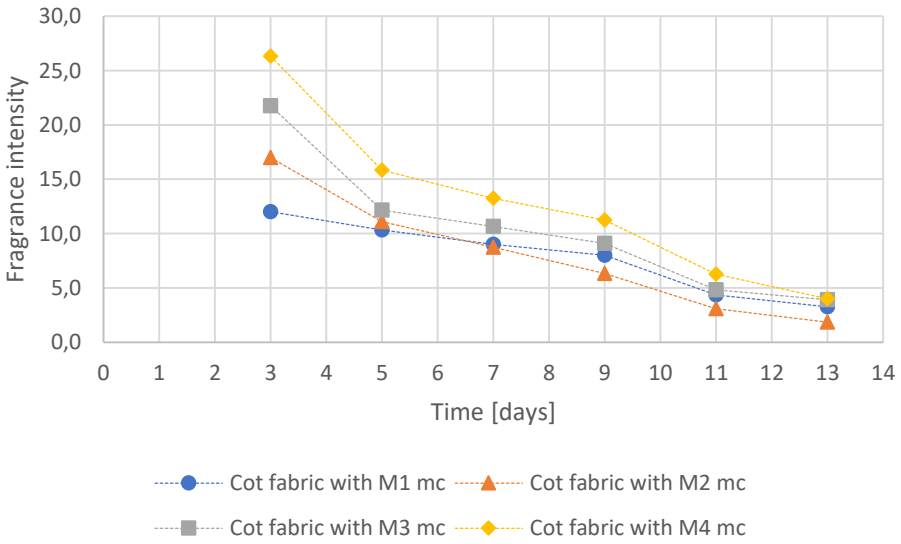


Figure 6 Fragrance intensity of microcapsule treated fabrics after certain periods of time

Table 4 The microcapsule amount loaded by the fabric and the microcapsule loading efficiency of the fabric

Microcapsule lot used for fabric treatment	Cinnamon oil content [g]	Microencapsulation efficiency [%]	Microcapsule amount used to treat the fabric [g]	Microcapsule amount loaded by the fabric [g]	Microcapsule loading efficiency of fabric [%]
M1	0.15	49.76	0.187	0.131	0.70
M2	0.25	49.15	0.194	0.148	0.76
M3	0.35	43.18	0.179	0.126	0.70
M4	0.45	37.24	0.162	0.102	0.63

Table 5 Fragrance intensity per gram of microcapsule loaded to the fabric

Microcapsule lot used for fabric treatment	Cinnamon oil content [g] in the microencapsulation formulation	Fragrance intensity per gram of microcapsule loaded to the fabric					
		After 3 days	After 5 days	After 7 days	After 9 days	After 11 days	After 13 days
M1	0.15	91.6	78.9	68.7	61.1	33.1	24.8
M2	0.25	114.9	74.9	59.1	42.8	20.8	12.4
M3	0.35	172.6	96.6	84.7	72.1	38.4	31.1
M4	0.45	258.2	155.2	129.9	110.3	61.3	39.2

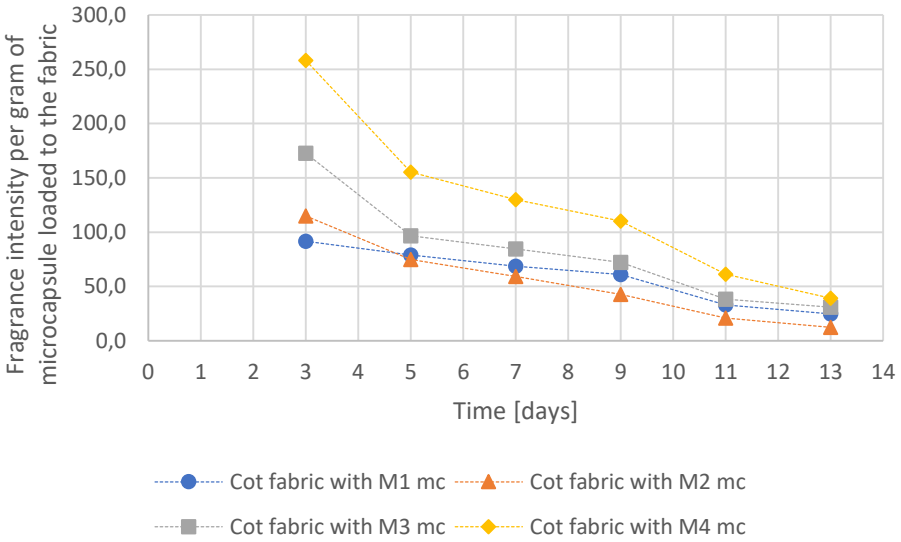


Figure 7 Fragrance intensity per gram of microcapsules loaded the fabric after certain periods of time

The fragrance intensity per gram of microcapsule was deduced from the fragrance intensity reported by experts and the microcapsule amount in gram loaded to the fabric and the results were given in Table 5 and Fig. 7.

The results at Table 5 and Fig. 7 also confirmed the higher efficiency in creating fragrance of microcapsule lot with higher cinnamon oil content used for the microencapsulation. Especially for the case of fabric treated with M4 microcapsules, with the minimum of microcapsule amount on the fabric (0.102 g, as in Table 4), after 3 days of release, the fragrance intensity (26.3, as in Table 3 and Fig. 6) as well as the fragrance intensity per gram of microcapsules loaded to the fabric (258.2, as in Table 5 and Fig. 7) were both the highest among the four microcapsule lots. It could be deduced that more oil content used in the microencapsulation helped to create higher oil loading of the elaborated microcapsules.

However, using less cinnamon oil content helped to prolong the fragrance on the fabric. As presented in Table 5 and Fig. 7, from the day of 3 to the day of 13, the fragrance intensity per gram of M1 microcapsules decreased from 91.6 to 24.8 (3.7 times) while this of M4 microcapsules decreased by 6.6 times (from 258.2 to 39.2).

As mentioned above, with more oil content used in the microencapsulation process, the elaborated microcapsules had smaller diameter with more porous polymer shell. The smaller microcapsules provided larger total surface area for the cinnamon oil to evaporate gradually from the microcapsule core out to the surrounding environment. Besides, the more porous polymer shell with larger holes on the surface (SEM images at Fig. 2) did help the cinnamon oil to release more easily and quickly. Therefore, the increase of cinnamon oil content used in the microencapsulation gave the fabric stronger fragrance intensity but faster decrease of it.

3.2.3 Influence of core - shell ratio on the antibacterial activity of fabric containing microcapsules

The antibacterial property is a major advantage of cinnamon oil for the textile application. Therefore, the change in antibacterial activity of the cotton interlock fabric treated with microcapsules according to the cinnamon oil content in the microencapsulation was necessary to be investigated. The antibacterial capability of the microcapsule treated fabric was expressed by the E. coli bacteria reduction [%] after 24 hours of incubation the fabric with bacterial suspension. The results were given at the Table 6.

The data at Table 6 indicated that untreated fabric had no antimicrobial activity and the treatment with microcapsules did improve the antimicrobial property of the fabric. However, only the fabrics treated with M1 and M2 microcapsules could inhibit

the growth of E. coli bacteria while the fabrics treated with M3 and M4 microcapsules could not.

Table 6 Antibacterial property of cotton interlock fabric treated with microcapsules

Sample	E. coli bacteria reduction [%]
Control sample (untreated fabric)	0
Fabric treated with M1 microcapsules	50
Fabric treated with M2 microcapsules	24
Fabric treated with M3 microcapsules	0
Fabric treated with M4 microcapsules	0

The fabric treated with M1 microcapsules (0.15 g) of cinnamon oil used in the microencapsulation) showed the best antimicrobial activity with 50 % of E. coli bacteria reduction. The result of antimicrobial activity could be attributed by the microcapsule morphology on the fabric surface after treatment as shown in Fig. 4. The more oil content used in microencapsulation, the more deflated and aggregated microcapsules on the fabric surface. The aggregation of microcapsules as well as the more wrinkle microcapsule shell with smaller holes limited contact between bacteria suspension and the oil deep in microcapsule core. Especially, in case of fabrics treated with M3 and M4 microcapsules, the strong deformation of microcapsules on the fabric surface (Fig. 4) and too wrinkle microcapsule shell (Fig. 5) was the reason for no antibacterial activity. On the other hand, quicker release of cinnamon oil from M3 and M4 microcapsules as reported in the part 3.2.2 above could be another reason. Moreover, the warm temperature (37 ± 1 °C) in the incubator accelerated the evaporation of cinnamon oil from the microcapsules, resulting in the lack of oil retained on the fabric test sample for enough antimicrobial activity.

4 CONCLUSIONS

The cinnamon oil was successfully encapsulated into eudragit RSPO microcapsules by solvent evaporation method. The microcapsules possessed spherical shape with the size range of 27 ÷ 48 μm. The microcapsules could be loaded to the interlock cotton fabric by impregnating technique with drying conditions at relative air humidity of 20% and temperature of 8 °C. The odor of cinnamon oil and the antimicrobial activity against E. coli strain was added to the fabric after microcapsule treatment.

The core - shell ratio in the microencapsulation process was changed in an increasing order of 1/2.3; 1/2; 1/1.7; and 1/1.5 by changing the cinnamon oil content with four levels of 0.15, 0.25, 0.35, and 0.45 g. The results showed close dependence of some microcapsule characteristics and some fabric properties on the cinnamon oil content.

The increase in cinnamon oil content made the decrease in microcapsule size, the microcapsules became more porous, more deformed, and more aggregate while the microencapsulation efficiency decreased slightly.

The increase in cinnamon oil helped to increase the fragrance intensity of the microcapsule treated fabric. The fragrance was still being felt after 13 days of oil release from the fabric. However, more oil used in the microencapsulation induced stronger deformed of microcapsule shell after the fabric treatment, resulting in the decrease in antimicrobial activity of the fabric. The fabric treated with M1 microcapsules (0.15 g of cinnamon oil was used) exhibited the best antimicrobial ability with E. coli reduction of 50%, while the fabrics treated with M3 and M4 microcapsules did not work.

In conclusion, for the application in fragrant and antimicrobial textile, within the scope of this research, M1 microencapsulation protocol with 0.15 g of cinnamon oil used was recommended due to the microcapsule spherical shape remained after the fabric treatment, the ability of releasing odor gradually until 13 days and the best antimicrobial property against E. coli bacteria.

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