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TEXTILE-BASED FOOTWEAR LININGS FUNCTIONALIZED WITH LAUREL OIL MICROPARTICLES: ANTIMICROBIAL PROTECTION

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The aim of this study is to optimize the production of microparticles to be used in antibacterial footwear linings and to characterize their usage and antibacterial properties. In this study, laurel essential oil was encapsulated with a chitosan shell using the spray drying method. The microparticles were applied to different lining materials using the dip-coating method. Scanning electron microscopy was used to characterize the microparticles and treated textile surfaces. The produced microparticles were characterized using scanning electron microscopy and particle size analysis. The finishing solution containing either laurel essential oil or laurel essential oil microparticles was applied to three different lining materials using the dip-coating method. After the finishing process, the lining materials were washed according to standards. The binding capacities of the microcapsules on different types of lining materials were determined using UV-Visible spectrophotometry, and their release properties were examined. Antibacterial tests were conducted to determine the antibacterial capacity of the final product and its effectiveness against washing.

Keywords: microencapsulation, laurel oil, footwear lining

INTRODUCTION

Today, consumers' interest in hygiene and active lifestyles is creating new challenges for the footwear industry. Footwear, with its close contact with the foot, provides an ideal breeding ground for bacteria and fungi due to the combination of moisture, warmth, nutrients from sweat, and oils from insoles (Orlita, 2004). Another important aspect of the modification of footwear components is the antimicrobial activity of the materials. Microbiological cleanliness inside the shoe is one of the factors that reduce the likelihood of dermatoses, ulcers, or other infections. Under actual usage conditions, footwear materials act as a barrier against the flow of moisture and temperature. Therefore, when water accumulates on the skin and lining materials, the temperature rises, and these specific conditions can affect the foot microbiome in the enclosed area around the foot (Serweta *et al*., 2019).

Microencapsulation, a prevalent technique, allows for controlled release of active substances, safeguarding them from adverse reactions over extended periods (Yalçın, 2020). Encapsulation involves embedding active molecules within a polymer structure, presenting a challenge in selecting suitable components. Spray drying, a widely employed microencapsulation method in the industry, offers cost-effective production, simplicity, and the ability to produce microparticles with desirable properties. It serves as an important commercial process for encapsulating various substances like vitamins, minerals, flavorings, and enzymes, providing economic and effective protection (Naveena, 2020).

Essential oils are known for their antifungal, antibacterial, antioxidant, antiviral and medicinal properties (Snuossi *et al*., 2016). When used directly, natural oils can stain textile products and cause allergic reactions on the skin. In addition, since the washing resistance is

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limited, microencapsulation studies are being carried out to overcome these disadvantages. (Türkoğlu, 2020). Laurel essential oil (*Laurus nobilis* L.) is an important plant of the genus Laurus, one of the 40 species in the *Lauraceae* family, and grows naturally in many temperate and warm regions, especially in Mediterranean countries such as Türkiye, Greece, Portugal, Morocco or Mexico (Yilmaz, 2013). Commercial essential laurel oil has a fresh camphor-aromatic odor with a spicy note and is a pale yellow to pale olive green in colour (Alfonso, 2017). Laurel essential oil obtained from nobilis leaves has been used in many fields including perfumes, cosmetics, phytotherapy, spices and nutrition (Merghni, 2016). The laurel oil has antibacterial, anti-infectious, analgesic, antiviral, and antiseptic qualities (Nesrine, 2018).

In this study, the spray drying method, known for its high encapsulation efficiency and speed, was used to encapsulate laurel essential oil. The produced microparticles exhibited a highly spherical shape, a rare occurrence with this method, attributed to optimized emulsion preparation processes. The microparticles were characterized using techniques such as scanning electron microscopy (SEM), particle size measurement, and production yield evaluation. The selected optimum microparticle formulation and the non-encapsulated laurel oil solution were applied to three different lining materials using the dip-coating method. After the finishing process, the lining materials were washed according to standards. To determine the binding capacities of the microcapsules on different types of lining materials, quantification and release properties were examined using UV-Visible spectrophotometry. The antibacterial capacity of the final product and its effectiveness against washing were determined through antibacterial tests.

MATERIALS AND METHODS

Materials

In the microencapsulation process, chitosan with a molecular weight of 600,000-800,000 (Acros Organics) was used as the encapsulating polymer at a 1% (w/v) concentration. Laurel oil was donated by Ephesus Spice & Essential Oil, Türkiye. Acetic acid (glacial) was procured from Merck (Germany), while Tween 40 (Fisher Scientific, UK) and Span 20 (Merck Millipore Corporation, Spain) acted as surface-active agents. TANAPUR One, a self-crosslinking polyurethane-based binder, is manufactured by Tanatex Chemicals (Netherlands), and PERIWET ELR, a wetting agent donated by Dr. Petry (Germany). Sodium carboxymethyl cellulose (Sigma-Aldrich, Merck, Germany) served as a thickening agent and dispergator. All other auxiliary materials used in the study are of technical quality.

Textile Materials

Three different footwear lining materials were employed in the research and the properties are presented in Table 1.

Table 1. Characteristics of footwear lining materials

Name	Lining material	Weight (g/m^2)	No of Layers	Lining material properties		
				Outer Layer	Middle Layer	Bottom Layer
Lining 1		350	1	100% raw cotton woven fabric		
Lining 2		400	2	100% PET woven	-	100% cotton nonwoven
Lining 3		400 (L1: 200 L2: 160 L3: 40)	3	70% PA + 30% PET Weft Knitting	100% PET Weft Knitting Heat laminated	100% PET Weft Knitting

Method

Microparticles were obtained by spray drying method in different proportions of chitosan and laurel essential oil. For this purpose, first of all, a 1% chitosan solution was prepared in a 2% acetic acid solution. Then, a determined amount of laurel essential oil was added to the prepared solution and homogenized using IKA T25 digital Ultra Turrax (Germany) (14,000 rpm for 20 minutes). The solutions prepared in different concentrations were sprayed from the 0.5 mm nozzle and fed into the desiccant chamber to form microparticles. It was prepared by using Unopex B 15 Mini Spray Dryer (Turkey). Chitosan: Laurel oil ratios have been studied as 1:1, 2:1 and 1:2 (w/w) ratios. In addition, various surfactant ratios have been tried to ensure emulsion stability, reduce capsule agglomeration, and improve particle size distribution. The optimal formulation was determined as the 1:1 Chitosan: Laurel oil formulation containing 20% surfactant. Spray drying conditions: the inlet temperature was 170 °C, the outlet temperature was 105 °C, and the pump speed was 5 mL/min.

Table 2. Application parameters

	Binder (g/L)	Capsule (g/L)	Laurel oil (g/L)
Solution 1	-	-	10
Solution 2	-	-	20
Solution 3	5	10 L_5	-
Solution 4	10	20 L_5	-
Solution 5	5	10 Blank	-

Various methods have been considered to characterize microparticles. To calculate the production efficiency, the amount of microparticles obtained was proportioned as a percentage of the theoretical amount of material added to the process solution. Scanning electron microscope (SEM) images were taken to examine the capsule morphology, which indicates ideal capsule formation. In addition, the size distribution analysis of the microparticles containing and not containing Laurel oil was performed. The optimum microparticle formulation was applied by immersion dip-coating method to different textile structures used as footwear linings. The composition of the process solutions is given in Table

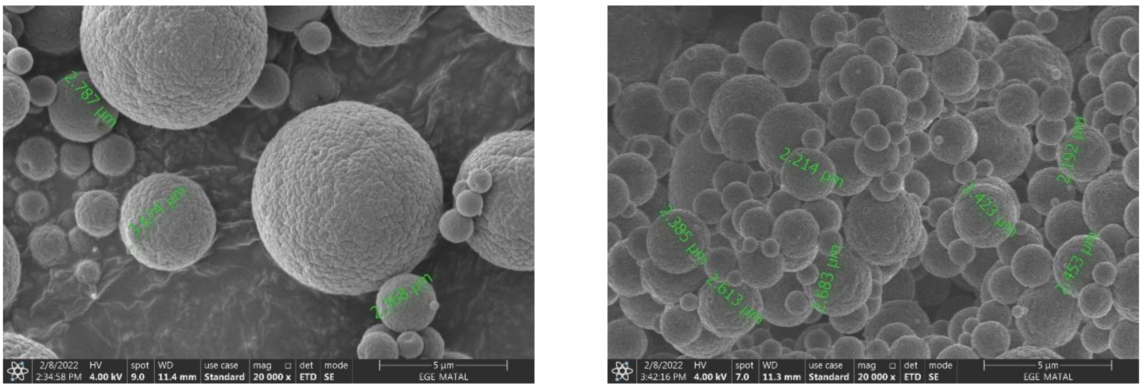
2. 1% CMC and 1% wetting were added to the finishing solutions. After the finishing process, the textile-based footwear linings were dried at 80 °C and the fixation process was applied at 120 °C. The footwear lining materials were washed according to ISO 105-C06:2010 standard 3 times in 30 °C for 30 min at Linitest Washing Machine with IEC Non-Phosphate Reference Detergent (A).

A standard line was plotted using a UV-Vis spectrophotometer to determine the laurel oil trapped in textile materials. Laurel oil was dissolved in various concentrations in n-hexane and the absorbance values of the prepared solutions were determined using a UV-Vis Spectrophotometer at a wavelength of 268 nm. The declaration of the standard line was calculated as $y=(5.62\times10^{-2})x+(8.96\times10^{-3})$, R^2 value was calculated as 0.99. In order to determine the adhesion capacities of laurel oil in different types of linings, the unwashed and three consecutive washed lining fabrics were extracted using n-hexane. After the solutions were filtered with a 0.45 µm membrane filter, measurements were made with a UV-Vis Spectrophotometer.

The antibacterial properties of footwear lining materials were evaluated by agar disk diffusional method. The antibacterial and antifungal properties of textile-based lining materials containing laurel oil have been determined for *Staphylococcus aureus* ATCC 29213, *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* ATCC 27853 and *Candida albicans* ATCC 90028. The textile samples were placed in petri dishes and incubated at 37 °C for 24 hours. Antimicrobial activity was determined by measuring the zone diameters formed around the samples after incubation.

RESULTS

The production efficiency of different microparticles obtained by spraying method ranges from 10 to 42. Among these formulations, especially the formulation containing 1:1 ratio of Laurel essential oil with chitosan and 20% surfactant exhibited significant advantages such as a particle size ranges from 5 to 100 µm, more homogeneous particle distribution and higher production efficiency compared to other microparticles. SEM images of microparticles are given in Figure 1. When the images were examined, it was seen that the shapes of the chitosan microparticles containing laurel oil were spherical, and the capsule wall was close to smooth.



Chitosan Microparticles **Chitosan Microparticles with Laurel Oil**

Figure 1. SEM images of microparticles

Color measurements were made using the CIELAB color space and significant color changes were detected in the footwear linings according to the ΔE values. The L* (lightness) values of all linings have generally decreased. It was determined that the total color change

(ΔE) of only laurel oil applied footwear lining materials was higher than capsule applied footwear lining materials. While the b* value increased in the direction of yellowness, textile linings containing microparticles usually exhibited the orange color of chitosan. There was no significant effect of capsule color on the L*. Lining 3, containing 20 g/L laurel oil (Solution 2), showed the greatest loss of lightness value. Redness (a*) was towards greenness, while the b* value increased in all solutions to the yellowness direction.

Table 3. Values of research lining materials

Sample	CIE Lab Values					ΔE
	L*	a*	b*	C*	H*	
Lining 1 -	82.061	2.126	13.134	13.305	80.808	
Lining 1 Solution 1	78.354	2.836	15.404	15.663	79.569	4.404
Lining 1 Solution 2	79.558	2.620	14.125	14.366	79.493	2.737
Lining 1 Solution 3	82.076	2.081	11.276	11.466	79.543	1.859
Lining 1 Solution 4	81.688	1.756	13.072	13.189	82.349	0.529
Lining 1 Solution 5	79.941	2.273	14.177	14.359	80.892	2.367
Lining 2 -	29.708	2.849	8.012	8.503	70.425	
Lining 2 Solution 1	27.370	2.635	7.882	8.311	71.514	2.351
Lining 2 Solution 2	27.293	2.529	8.056	8.444	72.574	2.437
Lining 2 Solution 3	28.331	2.192	6.932	7.270	72.454	1.869
Lining 2 Solution 4	27.491	2.489	7.486	7.889	71.611	2.307
Lining 2 Solution 5	26.177	2.314	7.428	7.780	72.695	3.619
Lining 3 -	52.432	-2.385	1.913	3.058	51.263	
Lining 3 Solution 1	51.048	-2.246	2.148	3.107	46.275	1.411
Lining 3 Solution 2	50.268	-2.162	2.576	3.363	40.001	2.274
Lining 3 Solution 3	51.786	-1.885	3.069	3.602	31.560	1.416
Lining 3 Solution 4	52.052	-1.981	3.964	4.431	26.550	2.125
Lining 3 Solution 5	50.345	-1.966	2.044	2.836	43.898	2.133

Table 4. The loading efficiency of laurel oil in different types of fabrics

	Solution 1	Solution 2	Solution 3	Solution 4	Solution 5
Lining 1	4.47 ± 0.10	3.66 ± 1.01	4.81 ± 0.21	3.11 ± 0.18	0.0 ± 0.0
Lining 1 - 3 Washes	0.958 ± 0.014	0.786 ± 0.005	0.514 ± 0.010	0.739 ± 0.010	0.0 ± 0.0
Lining 2	6.29 ± 0.67	3.50 ± 0.39	4.98 ± 0.58	3.95 ± 0.03	0.0 ± 0.0
Lining 2 - 3 Washes	2.417 ± 0.010	2.102 ± 0.005	1.237 ± 0.015	1.614 ± 0.010	0.0 ± 0.0
Lining 3	4.03 ± 0.29	5.97 ± 0.52	6.33 ± 1.01	5.12 ± 1.61	0.0 ± 0.0
Lining 3 - 3 Washes	1.142 ± 0.010	0.970 ± 0.000	0.902 ± 0.014	2.565 ± 0.005	0.0 ± 0.0

The loading efficiency of laurel oil in linings with Solution 3 is higher than in linings treated with other solutions. After three washes, the essential oil ratio has decreased, but there is still essential oil content in the fabric. All the linings can retain the essential oil in their structure. No significant difference was observed between fabrics treated with essential oil and those treated with microcapsules.

The antimicrobial test results obtained by the disk diffusion method showed that the application of laurel oil on the medium exhibited antibacterial activity against all test organisms, with the largest inhibition zones observed on *C. albicans*, confirming the oil's strong antifungal properties. These findings highlight the potential of laurel oil as an effective antimicrobial agent in various applications. However, no inhibitory effect on the growth of microorganisms was observed for chitosan capsules containing laurel oil and chitosan capsules without laurel oil against standard bacterial and yeast strains.

CONCLUSIONS

This study aims to develop various textile-based footwear linings using laurel oil-containing microparticles. In the production of capsules, chitosan polymer with antibacterial properties was used as shell material. Spray drying has been selected as a suitable method for industry and has been preferred in capsule production. Laurel oil has been selected for the control of bad odor of microbial origin that may occur in footwear due to its antimicrobial properties and pleasant smell. Laurel oil is strongly antibacterial on all test organisms, and especially it has shown significant antifungal effects on *Candida albicans*. The products developed are suitable for industrial production and laurel oil has the potential to be used as an effective antimicrobial agent.

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