Microencapsulated antimicrobials on non-woven textiles for shoe insoles

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Introduction

Microencapsulation technologies offer many opportunities to improve the properties of textiles, or to give them new functions.

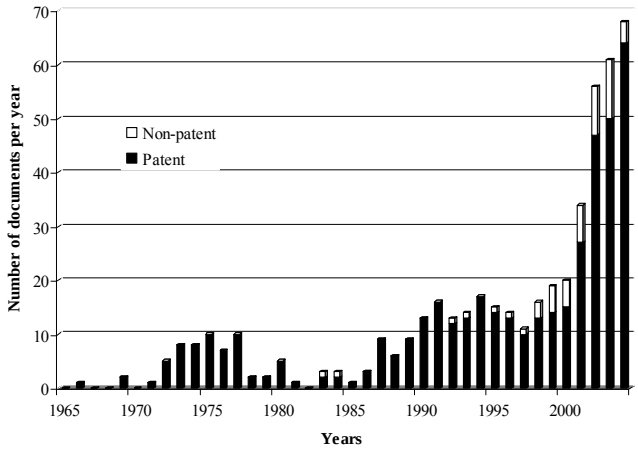

Figure 1: Bibliometric analysis of microencapsulation applications in textiles: yearly growth of new patents *vs.* non-patent documents in the Chemical Abstracts Plus database.

Bibliometric analyses show that the vast majority of publications on microencapsulation for textile applications are patents (Figure 1), illustrating the importance of industrial property rights in this specialized field. The first wave of microcapsule inventions for textiles was characteristic of the 1970s and introduced microencapsulated dyes, pigments, softeners, antistatic agents and fire retardants for textiles, while the second wave of inventions in the 1990s brought thermochromic and photochromic materials, antimicrobials, insect repellents, cosmetic and medical textiles. The third wave, biggest of all, took rise after the year 2000, and covers primarily the microencapsulated phase change materials for active accumulation and release of heat.

Patents describe different ways of incorporating microcapsules onto or into textiles: by spraying, by coating with an air knife or rod coater, by impregnation or immersion during the stage of chemical treatment, or by incorporation into plastic carriers, such as polymer foams, coatings and multilayer composites, followed by insertion into selected parts of textile clothing. In rare cases, microcapsules are incorporated directly into textile fibres during the spinning process. In a typical example, a suspension of microcapsules has to be formulated for applications on woven or nonwoven textiles. Formulation additives usually consist of binders, organic or inorganic pigments and fillers, antifoaming agents, and viscosity controlling agents.

This acticle describes the development of non-woven textiles, used for shoe insoles with prolonged antimicrobial activity. Textiles are impregnated with pressure-sensitive microcapsules, which release the active ingredient upon pressure during walking.

Materials and methods

Partly methylated trimethylolmelamine and a hexamethoxymethylolmelamine resin (both Melamin, Slovenia) were used as prepolymers for microcapsule walls. Styrene-maleic acid anhydride copolymer with average mol. weight 350,000 (Hercules) was used as a modifying agent and emulsifier for *in situ* polymerisation. Analytical grade sodium hydroxide (Kemika, Croatia) and sodium metabisulphite $Na_2S_2O_5$ (BASF) were used for termination of the polymerisation reaction and removal of free formaldehyde from the suspension of microcapsules. Essential oils of lavender (*Lavandula sp.)*, rosemary (*Rosmarinus officinalis) and* sage (*Salvia officinalis)* in mixtures with

isopropylmyristate as a solvent were used as antimicrobial active agents. Concentrations of 10%, 25% and 40% essential oil in the solvent were microencapsulated. Polyester, polypropylene and cellulose-polypropylene non-woven textiles (types of 30, 40, 45 and 250 g/m^2) were used as textile carriers for the shoe insoles. Acrylic latex, styrene-butadiene latex, and water-soluble binders - polyvinyl alcohol and carboxymethyl cellulose - were added as binders to microcaspsule suspensions prior to textile impregnation.

A modified *in situ* polymerisation method by (Knez E., 1995; Kukovič M. and Knez E., 1997) was used as the basic microencapsulation process for the preparation of microcapsules with melamine-formaldehyde prepolymers as a wall material, and a styrene-maleic acid anhydride copolymer as a modifying agent. The latter served both as an emulsifier and as a polycondensation initiator, which enabled the polymerisation to develop only at the surface of the emulsified oil droplets (future microcapsule cores), and not throughout the whole water phase (Figure 2).

For the impregnation of non-woven textiles with microcapsule formulations, a technique for the transport of the textile carrier through the impregnation basin was used (Figure 3).

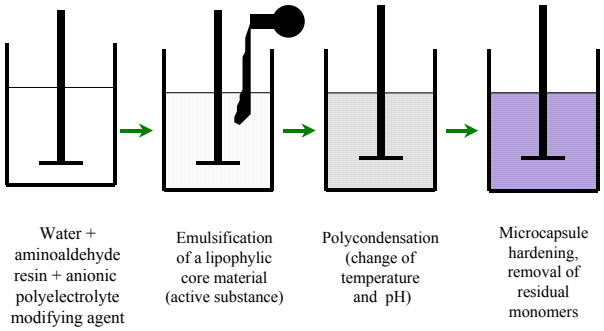

Figure 2: Microencapsulation by *in situ* polymerisation of amino-aldehyde resins

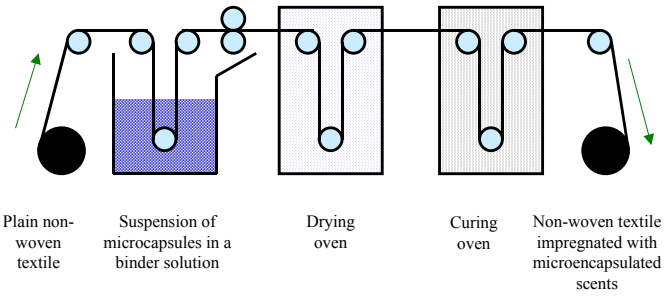

Figure 3: A process for preparing non-woven textile carriers saturated with microencapsulated essential oils

Headspace gas chromatography was used for the determination of quantities of essential oil in new and in worn textile shoe insoles. Textile insole samples containing microencapsulated essential oils were put into measuring flasks and exposed to elevated temperature at 160^{o}C for 45 min. Gaseous phases were then analysed by gas chromatography, using internal standards (flame-ionisation detector, capillary column HP Ultra 1 and HP Carbowax M20, initial temperature 60^{o}C, temperature gradient 2.5^{o}C/min, final temperature 190^{o}C).
Mechanical testing of shoe insoles was performed by walking (experimental person 80 kg), on average 3 km per day, for a total distance of 50 km.
The antimicrobial activity of shoe insoles made of non-woven textiles impregnated with microencapsulated antimicrobial essential oils was tested by a standard method for the determination of antibiotic activity. Clinical isolates of *Trichophyton mentagrophytes*, *Candida albicans, and Staphylococcus aureus* were used as reference microorganisms. The tests were performed with 10% and 40% concentration of essential oils in isopropylmiristate, and with the following further dilutions 1:2, 1:4, 1:8, 1:16, 1:32, 1:64, 1:128, 1:256, 1:512 and 1:1024.

Results and discussion

Impermeable pressure-sensitive microcapsules containing mixtures of sage, lavender and rosemary essential oils were produced in a 10 L reactor (Figure 4), and applied onto non-woven textiles (500g of microcapsule suspension/m^2) by immersion impregnation (Figure 5). Shoe insoles were produced from dried impregnated textiles (Table 1).

Parameter	Value
• melamine-formaldehyde prepolymer	11 g/100g of core material
• modifying agent/microcapsule core	6.5 g/100g of core material
• diameter of dissolver plate	80 mm
• rpm	1500 min^{-1}
• emulsification time	20 min
• share of dispersed phase in emulsion	35 vol%
• polymerisation time	90 min
• polymerisation temperature	75 °C

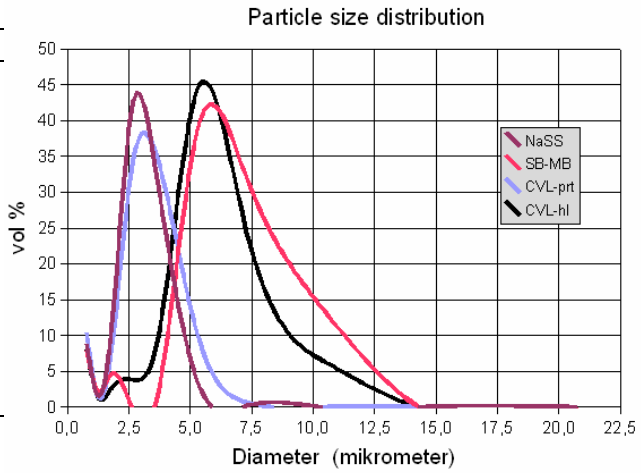

Figure 4: Main parameters of i*n situ* polymerisation microencapsulation in a 10 L reactor, and size distribution of four batches of pressure-sensitive microcapsules containing a mixture of essential oils (small microcapsules peak 2,5 µm, large microcapsules peak 6,0 µm)

Table 1: An example of a composition analysis by gas chromatography: new shoe insoles made of a non-woven polypropylene textile impregnated with microencapsulated essential oil mixture of *Lavandula hybrida*, *Rosmarinus officinalis and Salvia officinalis* in isopropylmyristate under normal conditions and after the test of accelerated diffusion at 150 °C in a ventilated chamber for 6 hours

Normal conditions				Test of accelerated diffusion		
Components of the essential oil mixture in microcapsule core	**% in the microcapsule core (start)**	**g / m^2 of non-woven textile**	**mg /pair of shoe insoles (450 cm^2)**	**Essential oil component**	**Start (% in the microcapsule core)**	**After 6 hours (% in the microcapsule core)**
α-pinene	1.10	1.54	69.30	α-pinene	1.037	0.201
camphene	0.85	1.19	53.55	camphene	0.749	0.498
sabinene	0.02	0.03	1.26	sabinene	0.495	0.086
β-pinene	0.37	0.52	23.31	β -pinene	0.182	0.000
1,8-cineol	3.60	5.04	226.80	1.8-cineole	0.582	0.074
limonene	0.81	1.13	51.03	limonene	3.529	3.843
α -thujone	0.93	1.30	58.59	thuyone	1.844	1.505
β -thujone	0.24	0.34	15.12	camphere	3.188	4.113
campherol	1.18	1.65	74.34	linalool	5.491	0.598
borneol	1.36	1.90	85.68	linalyl acetate	0.937	0.170
linalool	5.00	7.00	315.00	terpinene-4-ol	1.406	0.096
terpinene-4-ol	0.94	1.32	59.22	borneol	1.620	1.010
linalyl acetate	0.74	1.04	46.62	i-propylmyristate	75.163	82.604
cariophylene	0.25	0.35	15.75	other components	3.778	5.203
i-propylmyristate	74.00	103.60	4662.00	Total	100.000	100.000
other components	8.61	12.05	542.43			
Total	100.00	140.00	6300.00			

Chromatographic analyses, performed prior to and after the mechanical testing of shoe insoles, proved that antimicrobial essential oils were kept in the microcapsule core until the microcapsule wall was broken by a mechanical pressure during walking. Tests confirmed that microencapsulation of volatile essential oils enabled a sustained and prolonged release of essential oils from microcapsules during wearing of shoes. The results of headspace gas chromatograpy showed that after 50 km of walking, shoe insoles still contained 62 to 72 % of microencapsulated active ingredients. The release was more intense on insole parts exposed to higher mechanical pressure.

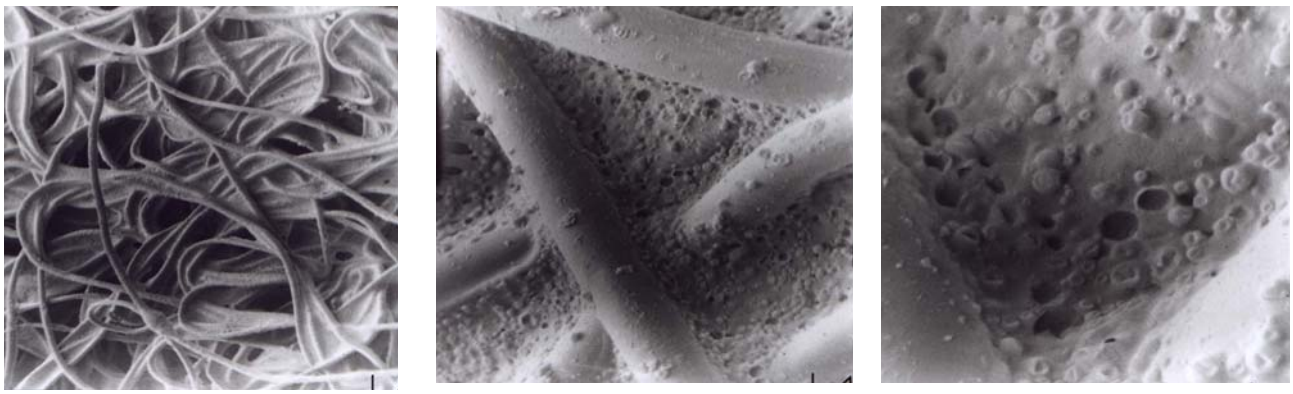

Figure 5: Scanning electron micrograph of a nonwoven textile shoe insole containing microencapsulated essential oils with antimicrobial properties (coated C + Au/Pd), 190x, 630x, 1900x

In *in vitro* antimicrobial activity tests against *Staphylococcus aureus,* a non-encapsulated mixture of 40% essential oil and 60% isopropyl miristate (solvent) was proven to have bactericidal activity. Bacteriostatic activities of 40:60 mixtures were observed in dilutions from 1:1 to 1:1024 (0.42 mg/ml). For mixtures of 10% essential oil and 90% of isopropyl miristate, the bacteriostatic activity was evident in dilutions up to 1:128.
In vitro tests against *Candida albicans* showed a fungicide activity of 40:60 mixtures up to the dilution 1:128 (3.36 mg/ml), while the fungicide activity of 10:90 mixture was proven at the minimum concentration of 0.42 mg/ml.
For the clinical isolate of dermatophyte *Trichophyton mentagrophytes* a higher concentration was needed for the fungicidal effect; the 40:60 mixture was fungicidal in minimal concentration of 215 mg/ml. Isopropylmiristate, which was used as a solvent for dilution of essential oils, did not exhibit any growth inhibition effects on tested microorganisms.

Conclusions

Essential oils of lavender, rosemary and sage were microencapsulated into melamine-aldehyde resin pressure-sensitive microcapsules and impregnated onto non-woven textiles. The main goal of microencapsulating essential oils with antimicrobial properties for textile shoe insoles was to achieve a targeted release during walking and no release when the shoes were not worn. Gas chromatography tests confirmed that this goal was fully achieved. Microencapsulation enabled controlled release; oils were kept in the microcapsule core until the microcapsule wall was broken by a mechanical pressure during walking. After 50 km of walking, shoe insoles still contained 60 to 70 % of microencapsulated active ingredients. Antimicrobial activity of shoe insoles was proved *in vitro* by a standard method for the determination of antibiotic activity against clinical isolates of *Trichophyton mentagrophytes*, *Candida albicans, and Staphylococcus aureus*.

Acknowledgement

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