Microencapsulation of essential oils and phase change materials for applications in textile products

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The paper reports the development and testing of three types of microcapsules for applications in textile products, namely microencapsulation of antimicrobial essential oils of sage, lavender and rosemary for nonwoven textile shoe insoles; smell-based animal repellents for agricultural textiles, designed to protect plants against damage caused by deer and rabbits; and paraffinic phase change materials (PCMs) for active thermal control garments.

In situ polymerisation of melamine-formaldehyde prepolymers was used as the microencapsulation technology in all three cases, based on partly methylated trimethylene melamine and hexamethoxymethylmelamine resin as wall materials and a styrene-maleic acid anhydride copolymer as a modifying agent. The microencapsulation process was modified to achieve the desired characteristics of microcapsule walls (different permeability and sensitivity/resistance to pressure). Bibliometric trends in microencapsulation technology with special reference to textile industries have also been discussed with an overview of main application fields and uses of microencapsulated additives in textile products.

Keywords: Microencapsulation, Nonwoven, Phase change material

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1 Introduction
1.1 Microencapsulation Trends

Microencapsulation includes several technologies for coating micrometer sized particles of finely ground solids, drops of liquids, or gaseous components with protective spherical membranes — microcapsule walls. Microencapsulation can be considered as a typical example of a knowledge-intensive and dynamic research field with an increasing growth of publications (Fig. 1). Trends in patent vs. non-patent literature illustrate the growth of basic research (non-patent literature), and a faster growth of industrial research represented in waves of patented inventions.

Microencapsulation technologies offer many opportunities to improve the properties of textiles or to give them new functions. Bibliometric analyses show that the vast majority of publications on microencapsulation for textile applications are the patents (Fig. 2), illustrating the importance of industrial property rights in this specialized field. The first wave of microcapsule inventions for textiles broke out in 1970s and inroduced 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 covered primarily the microencapsulated phase change materials (PCMs).

Fig. 1—Yearly growth in new publications on microencapsulation in the Chemical Abstracts Plus database
1.2 Microencapsulation Processes

The selection of microencapsulation processes depends on the desired characteristics and uses of textile final products. The properties of microcapsules, their sizes, shapes, wall materials, active substance release mechanisms, method of application, and compatibility with formulation additives have to be adapted to the requirements of textile processing methods and uses of final products. The preparation of microcapsules for textile finishing compositions was initially based on coacervation processes and later on polymerisation methods, such as interfacial polymerisation and in situ polymerisation of aminoaldehyde resins.

The coacervation phenomenon takes place in colloid systems, where coacervate droplets (a macromolecular colloid rich phase) surround dispersed microcapsule cores and form a viscous microcapsule wall, which is then hardened with a cross-linking agent (Fig. 3a). In polymerisation methods, monomers polymerise around emulsified or dispersed cores and form a solid polymeric wall. In the interfacial polymerisation (Fig. 3b), one of the monomers is typically dissolved in the aqueous phase and the other in a hydrophobic solvent phase, while in the in situ polymerisation (Fig. 3c), monomers or precondensates are added only to the aqueous phase of the emulsion.

1.3 Microcapsule Formulations for Textile Applications

Patents describe different ways of incorporating microcapsules onto or into textiles, such as 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.

Binders play a crucial role in microcapsule coating formulations. They may be selected from the groups of water soluble polymers (e.g. starch and modified starches, carboxymethyl cellulose, polyvinyl alcohol, and xanthanes), synthetic latexes (e.g. styrene-
butadiene, polyvinylacetate or acrylate latexes with anionic and/or nonionic emulsifiers), aminoaidehyde resins (e.g. urea- and melamine-formaldehyde resins, dimethyl ethylene urea, dimethyl dihydroxy ethylene urea, and dimethyl propylene urea), and silicones.

1.4 Applications of Microcapsules in Textile Products

The idea of using microencapsulation technology in textile products was born soon after the first introduction of the industrial production of microcapsules for carbonless pressure-sensitive copying papers in the middle of the previous century. Possibilities of using microencapsulation technologies in textile products are numerous, and have already been described in detail. The main application fields and uses of microencapsulated additives in textile products are summarised in Fig. 4. The products include: dyes and pigments; ingredients for transfer printing; thermochromic materials; photochromic materials; catalysts and enzymes; fire retardants; sizing and bonding agents; blowing and expanding agents; waterproofing agents; detergent components, such as enzymes; bleaching and whitening additives; antifoaming agents; dry cleaning agents; softeners and antistatic agents; fragrances and perfumes; insect repellents; deodorants and disinfectants; active ingredients for cosmetic textiles; adsorbents and decontaminants; thermal regulation agents based on sunlight conversion; and heat storage materials based on phase change materials.

This paper describes microencapsulation of antimicrobial essential oils for shoe insoles, animal repellents for agricultural textiles, and PCMs for active thermal control garments. In situ polymerisation of melamine-formaldehyde resins was used as the microencapsulation technology in all three cases.

The idea of fragranced textiles containing microencapsulated essential oils and aromas is more than thirty years old. Aromatic capsules have been developed, which either slowly release their contents through semipermeable walls or have impermeable walls which burst open by mechanical pressure and rubbing when the wearer moves. A new generation of aromatic textiles entered the market when better washfast bind-

![Fig. 4—Applications of microcapsules in textile products](image-url)
ers were introduced. According to patent literature, these fragranced textile products retain the aroma over several years, keep the microcapsules over 25 washing cycles or resist dry cleaning. Typical products include fragranced garments, bed linen, and textiles for furniture and car interiors.

In addition to the pleasant aroma, several essential oils also possess antimicrobial, fungicidal and deodorant properties. Based on some essential oils, antibacterial printing compositions for garments and antimicrobial nonwoven textile shoe insoles with prolonged activity, based on pressure-sensitive microcapsules which release the active ingredient during walking, have also been developed.

Textiles with prolonged insect repellent effects have been developed to protect the wearer against mosquitoes and ticks, or to protect textiles by applying microencapsulated mothproofing agents. Applications include insect repelling carpets and curtains, panty hoses with durable insect repellence, sprays for mothproofing treatment, and animal repellent textiles for agricultural and horticultural uses. Similarly as in the case of microencapsulated fragrances, many improvements in microencapsulated repellents on textile supports deal with binders for improved wash fastness.

The fastest growing microencapsulation application in textiles has become sportswear and special technical apparel, based on microencapsulated PCMs with heat and cold absorbing capacity. Several firms compete for the intellectual property rights and market shares in this field. Sportswear shops are offering coats, jackets, boots, socks and gloves with the active thermal control technology.

PCMs are a sub-group of heat storage materials with a dynamic heat exchange process taking place at the melting point temperature. When a PCM undergoes a phase change transition from solid to liquid, energy is stored in the form of latent heat at a constant temperature. Accumulated latent thermal energy is then released when the PCM solidifies again. In general, the higher the PCM's latent heat of phase change is, the more thermal energy a material can store. The transition process is completely reversible. To overcome practical problems of solid-liquid phase transitions, PCMs are microencapsulated and turned into solid formulations or suspensions for applications in various thermal management applications. In textile applications, microcapsules with PCMs are incorporated into fabrics with enhanced thermal properties, functioning as heat absorbers or as barriers against cold. In heating PCMs, the temperature gradient flows from the PCM into the body, and the phase transition temperature is above the body's normal skin temperature. The cooling PCMs have a phase transition temperature below the body's normal skin temperature. When chilled below their transition temperature, the temperature gradient flows from the body into the PCM.

For garments that could better keep a constant temperature, microencapsulated PCMs were first incorporated in the fibres. The idea was further developed by several researchers, but it was difficult to incorporate enough PCM in the fibre structure to get a thermal result while retaining the fibre's mechanical characteristics. To overcome this problem, PCM microcapsules were incorporated into textile products in different ways, such as coated on fibres and fabrics with a binder or built into polymer foam inserts and composites with two or more layers. Several textile applications were then developed, such as improved diving suits, fire wear, special working clothes, military uniforms, gloves and shoes, leather products and special textile products containing electric heating circuits.

2 Materials and Methods

2.1 Materials

Partly methylated trimethylolmelamine and a hexamethoxytrimethylolmelamine resin (both procured from 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 Na2S2O7 (BASF) were used for the termination of polymerisation reaction and removal of free formaldehyde from the suspension of microcapsules.

Essential oils of lavender (Lavandula hybrida), 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.

Daphne (Dragoco, Austria) was used as an animal repellent, based on a mixture of essential oils and other volatile compounds. Its main components are vanillin, heliotropin (3,4-methylenedioxybenzaldehyde), cyclamaldehyde .3-(4-isopropyl-phenyl)-2-methylpropanal, methionyl acetaldehyde, citronellol (3,7-dimethyl-6-octen-1-ol) and dimethylphthalate as a solvent. Four paraffinic hydrocarbons (AGS, Turkey and Rubitherm,
Germany) with melting points 25°C, 28°C, 40°C and 50°C were used as PCMs for microencapsulation.

Polyester, polypropylene and cellulose-polypropylene nonwoven textiles (30, 40, 45 and 250 g/m²) were used as textile carriers for the shoe insoles with antimicrobial activity. Polypropylene nonwoven textiles (20 and 30 g/m²), and cellulose-polypropylene nonwoven textile (40 g/m²) were used as carriers for Daphne animal repellent microcapsules. The impregnated agricultural textiles were dried and cut into strips (length 3 m, width 5 cm).

Acrylic latex, styrene-butadiene latex, and water-soluble binders (polyvinyl alcohol and carboxymethyl cellulose) were added to microcapsule suspensions prior to textile impregnation.

2.2 Methods

A modified in situ polymerisation method 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 (Fig. 5).

The melting points of PCMs were determined by differential scanning calorimetry (Perkin Elmer Pyris-1). The microcapsule size and size distribution were measured by Coulter Counter TA II apparatus and by Alkatel Cilias Laser Granulometer 715. Aqueous suspensions of microencapsulated PCMs were dried by a Büchi B290 spray dryer. Scanning electron microscopy was performed by JEOL JSM-6060LV microscope at accelerating voltage 15 kV with microcapsule coating C + Au/Pd.

For the impregnation of nonwoven textiles with microcapsule formulations, a technique for the transport of the textile carrier through the impregnation basin was used (Fig. 6). Headspace gas chromatography was

![Fig. 5—Microencapsulation by in situ polymerisation of amino-aldehyde resins](image)

![Fig. 6—A process for preparing nonwoven textile carriers saturated with microencapsulated active agents](image)
used for the determination of quantities of essential oil in new and worn textile shoe insoles. Textile insole samples containing microencapsulated essential oils were put into measuring flasks and exposed to elevated temperature at 160°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°C, temperature gradient 2.5°C/min, and final temperature 190°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 nonwoven 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% concentrations of essential oils in isopropylmyristate, and with the further dilutions to 1:2, 1:4, 1:8, 1:16, 1:64, 1:128, 1:256, 1:512 and 1:1024.

Field testing of microencapsulated animal repellents on textile strips was carried out in the winter season on two agricultural fields near the forest. The pressure of wild animals on agricultural surfaces was strong in snow because the availability of natural food was very limited. The efficacy of the repellent agricultural textiles was studied on deer and rabbits. Textile carriers (3 m long and 5 cm wide) impregnated with microencapsulated repellent Daphne were tested using baits with 10 one-year-old apple branches in each bait (1 m long branches, 10 cm distance between branches, 150 m distance between baits); the methodology as described earlier was used. The number of damaged branches per bait (1-10) was used as the criterion to evaluate damage caused by animals.

3 Results and Discussion

3.1 Microencapsulated Antimicrobial Essential Oils for Textile Shoe Insoles

Impermeable pressure-sensitive microcapsules containing antimicrobial mixtures of sage, lavender and rosemary essential oils were successfully produced by the process described earlier and then applied onto nonwoven textiles by immersion impregnation. Shoe insoles were produced from dried impregnated textiles. An example of essential oil components present in non-ruptured microcapsules in a new polypropylene shoe insole, detected by the headspace gas chromatography, is given in Table I.

Chromatographic analyses, performed prior to and after the mechanical testing of shoe insoles, proved that the antimicrobial essential oils were kept in the microcapsule core until its wall was broken by a mechanical pressure during walking. Tests confirmed that the 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 chromatography showed that after 50 km of walking, shoe insoles still contained 62-72% of microencapsulated active ingredients. The release was more intense on insole parts exposed to higher mechanical pressure.

In in vitro antimicrobial activity tests against Staphylococcus aureus, a non-encapsulated mixture of 40% essential oil and 60% isopropyl myristate (solvent) was proven to have bactericidal activity. Bacte-
riostatic activities of above 40:60 mixtures were also observed using 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. Isopropyl miristate, which was used as a solvent for dilution of essential oils, did not exhibit any growth inhibition effects on tested microorganisms.

3.2 Microencapsulation of Animal Repellents for Agricultural Textiles

The main purpose of microencapsulating volatile animal repellents was to prolong their activity by slow diffusion through microcapsule walls. To achieve partly permeable microcapsule walls, process parameters had to be modified. An example of in situ polymerisation microencapsulation parameters for the preparation of Daphne repellent microcapsules in a 10 L reactor is given in Table 2.

Agricultural field testing showed a good repelling effect against deer and rabbits for both formulations of nonwoven textile strips impregnated with microencapsulated repellent Daphne. The results are given in Table 3 and Fig. 7.

### Table 2—Main parameters of in situ polymerisation microencapsulation of Daphne repellent in a 10 L reactor

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melamine-formaldehyde prepolymers</td>
<td>11 g/100g of core material</td>
</tr>
<tr>
<td>Modifying agent/microcapsule core</td>
<td>6.5 g/100g of core material</td>
</tr>
<tr>
<td>Diameter of dissolver plate</td>
<td>80 cm</td>
</tr>
<tr>
<td>Mixing speed</td>
<td>1500 rpm</td>
</tr>
<tr>
<td>Emulsification time</td>
<td>20 min</td>
</tr>
<tr>
<td>Share of dispersed phase in emulsion</td>
<td>35 vol. %</td>
</tr>
<tr>
<td>Polymerisation temperature</td>
<td>90 min</td>
</tr>
<tr>
<td>Polymerisation temperature</td>
<td>75°C</td>
</tr>
</tbody>
</table>

### Table 3—Animal repellent efficacy of nonwoven textiles impregnated with microencapsulated repellent Daphne—Field testing against deer and rabbit

<table>
<thead>
<tr>
<th>Evaluation day of experiment</th>
<th>Control (Untreated)</th>
<th>Impregnated textile 20g/m²</th>
<th>30g/m²</th>
<th>Control (Untreated)</th>
<th>Impregnated textile 20g/m²</th>
<th>30g/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
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</tr>
<tr>
<td>4</td>
<td>1</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>2</td>
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<td>3</td>
<td>0</td>
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</tr>
<tr>
<td>10</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>4</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>6</td>
<td>0</td>
<td>7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>10</td>
<td>10</td>
<td>8</td>
<td>8</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 4—Main process parameters for the preparation of PCM microcapsules in a 10 L reactor

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filling amount of PCM in emulsion</td>
<td>7 – 10 L</td>
</tr>
<tr>
<td>(microcapsule core)</td>
<td></td>
</tr>
<tr>
<td>Amount of PCM in emulsion</td>
<td>25 – 40%</td>
</tr>
<tr>
<td>Conc. of modifying agent</td>
<td>4 – 6.5%</td>
</tr>
<tr>
<td>Conc. of prepolymer (microcapsule wall material)</td>
<td>18.5 – 40 g/100 mL</td>
</tr>
<tr>
<td>Stirrer diameter</td>
<td>90 mm</td>
</tr>
<tr>
<td>Mixing speed</td>
<td>1000 – 2000 rpm</td>
</tr>
</tbody>
</table>

Table 5—Characteristics of four batches of microcapsules containing PCMs with the melting point of 25°C, 28°C, 40°C and 50°C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point of PCM in microcapsule core, °C</td>
<td>25 28 40 50</td>
</tr>
<tr>
<td>Mixing speed during emulsification, rpm</td>
<td>1500 1500 1900 1500</td>
</tr>
<tr>
<td>Av. diameter of microcapsules, μm</td>
<td>9.10 8.30 7.86 8.63</td>
</tr>
<tr>
<td>Av. thickness of microcapsule wall, μm</td>
<td>0.14 0.22 0.15 0.17</td>
</tr>
<tr>
<td>Microcapsule suspension dry matter, %</td>
<td>37.0 38.2 39.5 36.4</td>
</tr>
<tr>
<td>Microcapsule suspension viscosity at 25 °C (Brookfield), mPas</td>
<td>300 425 300 470</td>
</tr>
<tr>
<td>Microcapsule suspension pH</td>
<td>7.0 7.6 7.7 7.3</td>
</tr>
</tbody>
</table>

3.3 Microencapsulation of PCMs for Textile Applications

To remain functional over numerous phase transition cycles, microencapsulated PCMs have to remain encapsulated within the impermeable microcapsule walls for the whole product life. PCM microcapsules needed to be highly resistant to mechanical and thermal stress, which was achieved by the modifications of microencapsulation process.

In in situ polymerisation of amino-aldehyde resins, all materials for the microcapsule wall originate from the continuous (aqueous) phase, and therefore have to be water soluble. Under ideal conditions, by the change in pH or temperature all mass of the wall material precipitates and distributes evenly over the surfaces of droplets in emulsion (future microcapsule cores). This results in a uniform microcapsule wall thickness, regardless of the microcapsule size.

Fig. 8—Scanning electron micrograph (magnification x 8000) of microcapsules (3-6 μm diameter) containing paraffinic PCMs, obtained after the spray drying of the microcapsule suspension

Better process control and improved mechanical properties of PCM microcapsules were achieved primarily by the selection and optimisation of a combination of wall prepolymer (partly methylated trimethylolmelamine) and the modifying agent (styrene-maleic acid anhydride copolymer with the molecular weight of 350.00 g/mol), which had a double function of being an emulsifier and a polycondensation initiator for melamine-formaldehyde precondensates. At optimum conditions, polymerisation evenly developed at the surface of the emulsified PCMs, thus forming an impermeable microcapsule wall.

The process parameters for the microencapsulation of PCMs in a 10L reactor are given in Table 4, and the characteristics of microcapsules containing PCMs as the core material are listed in Table 5. The process enabled the production of microencapsulated hydrocarbon PCMs with mechanically and thermally stable amino-aldehyde walls and narrow particle size distribution (Fig. 8). By regulating the ratio of entering raw materials, it was possible to change the properties of microcapsule walls as well as to regulate the dry matter content, pH and viscosity of the final microcapsule suspensions.

4 Conclusions

Microencapsulation of antimicrobial essential oils, animal repellents and PCMs for textile applications has been described. In all three cases, a modified in situ polymerisation method was used for the preparation of synthetic polymeric walls. However, process parameters had to be modified and adjusted to achieve different release mechanisms. In the case of volatile
animal repellents, essential oils needed to be slowly released from the microcapsule core by diffusion/evaporation, to achieve a prolonged release; therefore the microcapsule wall had to be partially permeable. The main goal of microencapsulating antimicrobial essential oils for textile shoe insoles was to achieve a targeted release during walking and no release when the shoes were not worn. Microcapsule walls had to be impermeable and pressure-sensitive. In the case of microencapsulated PCMs, in addition to impermeability, an improved mechanical resistance of microcapsule walls was needed to assure a sufficient mechanical strength to withstand solid-liquid transitions of microcapsule core without leaking. Main process modifications to reach the desired microcapsule characteristics were based primarily on the selection and ratio of melamine-aldehyde prepolymers and of a styrene-maleic acid anhydride copolymer modifying agent, as well as on the determination of emulsification and polymerisation parameter (rpm, temperature, duration). Experiments in a 10l reactor showed that for each core material, process parameters had to be empirically optimised to achieve the desired characteristics.

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