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Microencapsulation for Textile Applications and Use of SEM Image Analysis for Visualisation of Microcapsules

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Abstract

The article presents the possibilities of using scanning electron microscopy (SEM) for the microencapsulation research purpose and for the visualisation of microcapsule applications on textiles. The laboratory and industrial scale synthesis of aminoplast microcapsules with in situ polymerisation of melamine-formaldehyde prepolymers, containing fragrances, essential oils and phase change materials (PCM) as core materials, is presented. The following properties of microcapsules were studied with the use of SEM in combination and in comparison with classical methods of microcapsule properties evaluation: (a) appearance, size and morphology of microcapsules, including the determination of wall thickness, (b) visualisation of fragrance and/or essential oils containing aminoplast microcapsules on non-woven and woven textile carriers, (c) evaluation of mechanical resistance of PCM microcapsule walls under pressure at an elevated temperature, and (d) detection of morphological changes of PCM microcapsules caused by ammonia scavenger. For graphical analyses, the processing of SEM images was performed with ImageJ software.

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Mikrokapsuliranje za tekstilno uporabo in uporaba analize SEM posnetkov za vizualizacijo mikrokapsul

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Izvleček

Prispevek predstavlja možnosti za uporabo elektronske vrstične mikroskopije (SEM) pri raziskovalnem delu na področju mikrokapsuliranja in za vizualizacijo mikrokapsul po nanašanju na tekstilije. Predstavljeni sta laboratorijska in industrijska sinteza aminoplastnih mikrokapsul z in situ polimerizacijo melamin-formaldehidnih prepolimerov za mikrokapsuliranje dišav, eteričnih olj in fazno spremenljivih materialov (PCM). Z uporabo SEM smo proučevali naslednje lastnosti mikrokapsul v kombinaciji in v primerjavi s klasičnimi metodami za evalvacijo mikrokapsul: (a) videz, velikost in morfologija mikrokapsul, vključno z določanjem debeline stene, (b) vizualizacija porazdelitve mikrokapsul z dišavami in/ali eteričnimi olji na netkanih in tkanih tekstilnih nosilcih, (c) evalvacija mehanske trdnosti PCM mikrokapsul pod pritiskom pri povišani temperaturi, (d) detekcija morfoloških sprememb mikrokapsuliranih PCM, ki jih povzroča dodajanje amoniaka kot lovilca ostankov formaldehida. Za grafično analizo SEM fotografij smo uporabili programsko opremo ImageJ software.

Ključne besede: mikrokapsule, tekstilije, vrstična elektronska mikroskopija SEM, slikovna analiza, morfologija, dišave, fazno spremenljivi materiali (PCM)

1 Uvod

1.1 Mikrokapsuliranje za tekstilstvo

Mikrokapsuliranje je proces, v katerem delce µm dimenzij obdamo z ovojnico, da pridobimo drobne kapsule s številnimi uporab-

Keywords: microcapsules, textiles, SEM image analysis, morphology, fragrances, phase change materials, textiles

1 Introduction

1.1 Microencapsulation for textiles

Microencapsulation is a process where the particles of µm dimensions are surrounded by a coating to produce small capsules with several useful properties. A container-type microcapsule is a small sphere with a liquid core (microcapsule core or fill, internal phase) and a uniform wall around it (shell, coating or membrane).

Industrial applications of microencapsulation were first introduced at the end of the 1950s in the production of pressure-sensitive copying papers for the encapsulation of leuco dyes [1]. Since then, microencapsulation has been constantly improved, modified and adapted for a variety of purposes and uses. In addition to the graphic and printing industries, microcapsules have been used for pharmaceutical and medical purposes, in cosmetic and food products, agricultural formulations, as well as in the chemical, textile and construction materials industries, biotechnology, photography, electronics, and waste treatment [2, 3].

Microencapsulation technologies offer many opportunities to improve the properties of textiles or to give them completely new functions. The first ideas of using microcapsules in textile products were born more than three decades ago (cf. Figure 1) and soon became a typical research field with a pronounced protection of industrial intellectual property rights. As a consequence, the number of patent applications strongly outnumbered scientific articles (cf. Figure 2).

Extensive and detailed literature reviews of microencapsulation applications in textiles have been published in previous works [4, 5, 6]. Typical examples of patented microcapsule applications in textile products (cf. Figure 3) include microencapsulated dyes and pigments for textile dyeing and printing, thermochromic and photochromic effects, microencapsulated catalysts and enzymes for special textile treatment, agents for textile sizing, adhesive bonding, wa-

nimi lastnostmi. Mikrokapsule rezervoarnega tipa so kroglice, ki imajo tekoče jedro (jedro mikrokapsule ali polnilo, notranja faza) obdano s steno (ovojnico, prevleko ali membrano).

Industrijska uporaba mikrokapsuliranja je bila vpeljana konec 50. let 20. stoletja za mikrokapsuliranje levko barvil v proizvodnji na pritisk občutljivih kopirnih papirjev [1]. Tehnologije mikrokapsuliranja nenehno izboljšujejo, spreminjajo in prilagajajo za različne namene in uporabo. Poleg tiskarske in grafične industrije mikrokapsule uporabljajo za farmacevtske in medicinske namene, v kozmetičnih in živilskih izdelkih, pripravkih za kmetijstvo, kot tudi v kemični, tekstilni in gradbeni industriji, biotehnologiji, fotografiji, elektroniki ter za ravnanje z odpadki [2, 3].

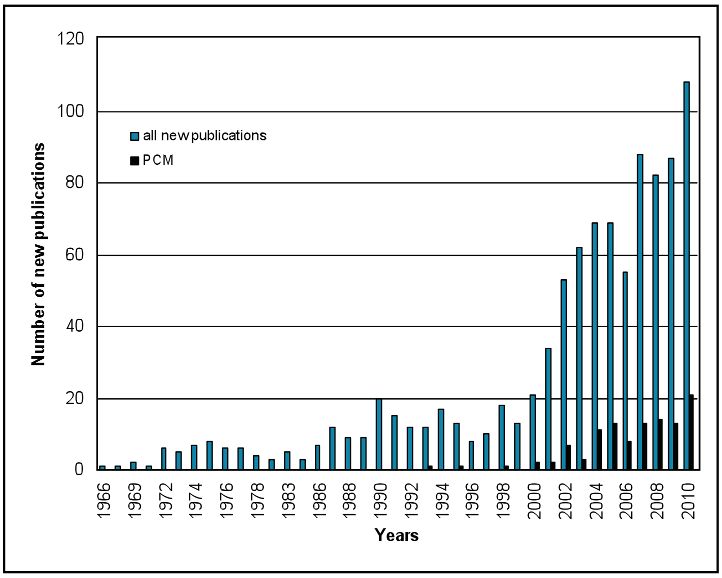


Figure 1: Trend of yearly new publications on microencapsulation in textiles and sub-segment of microencapsulated Phase Change Materials in textiles. Chemical Abstracts Plus database, search profile 1: (microencapsulation OR microcapsules) AND textile; search profile 2: (microencapsulation OR microcapsules) AND textile AND (phase change material OR PCM)

Tehnologije mikrokapsuliranja ponujajo številne možnosti za izboljšanje lastnosti tekstilij ali za pridobitev povsem novih lastnosti. Primeri patentiranih aplikacij mikrokapsul na tekstilnem področju so obstajali že pred tremi desetletji (slika 1) in tehnologija mikrokapsuliranja je postala zanimivo raziskovalno področje z naraščajočim številom patentnih prijav, ki so presegale število znanstvenih prispevkov (slika 2).

ter proofing, blowing agents for leather substitutes, softener and antistatic compositions, ingredients in textile detergents, microencapsulated textile fragrances, perfumes, fire retardants, and special functional textiles with microencapsulated insect repellents, antimicrobial, disinfectant and deodorant components, bioactive medical and cosmetic textiles and textiles for active thermal control with microencapsulated phase change materials (PCMs). One of the fastest growing microencapsulation applications in textiles during the last decade has become sportswear and special technical apparel, based on microencapsulated PCMs with heat and cold absorbing capacity (cf. Figure 1). 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 subgroup of Heat Storage Materials (HSMs) with a dynamic heat exchange process taking place at the melting point tempera-

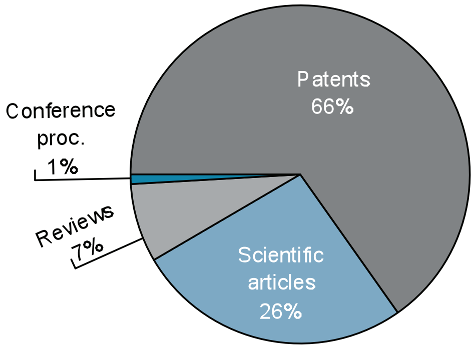


Figure 2: Publications on microencapsulation in textiles, analysed by document type. Chemical Abstracts Plus database, search profile: (microencapsulation OR microcapsules) AND textile

Obširnejše analize literaturnih virov s področja tehnologije mikrokapsuliranja v tekstilstvu so bile že objavljene [4, 5, 6]. Primeri patentiranih aplikacij so tekstilni izdelki z mikrokapsuliranimi barvili in pigmenti za barvanje tekstila (slika 3) in za tisk na tekstil, termokromni in fotokromni učinki, mikrokapsulirani katalizatorji in encimi za posebne obdelave tekstilij, sredstva za aprature, lepljenje, vodotesnost, penilci za umetno usnje, mehčalci in antistatiki, sestavine v pralnih praških, dišave, parfumi, zaviralci

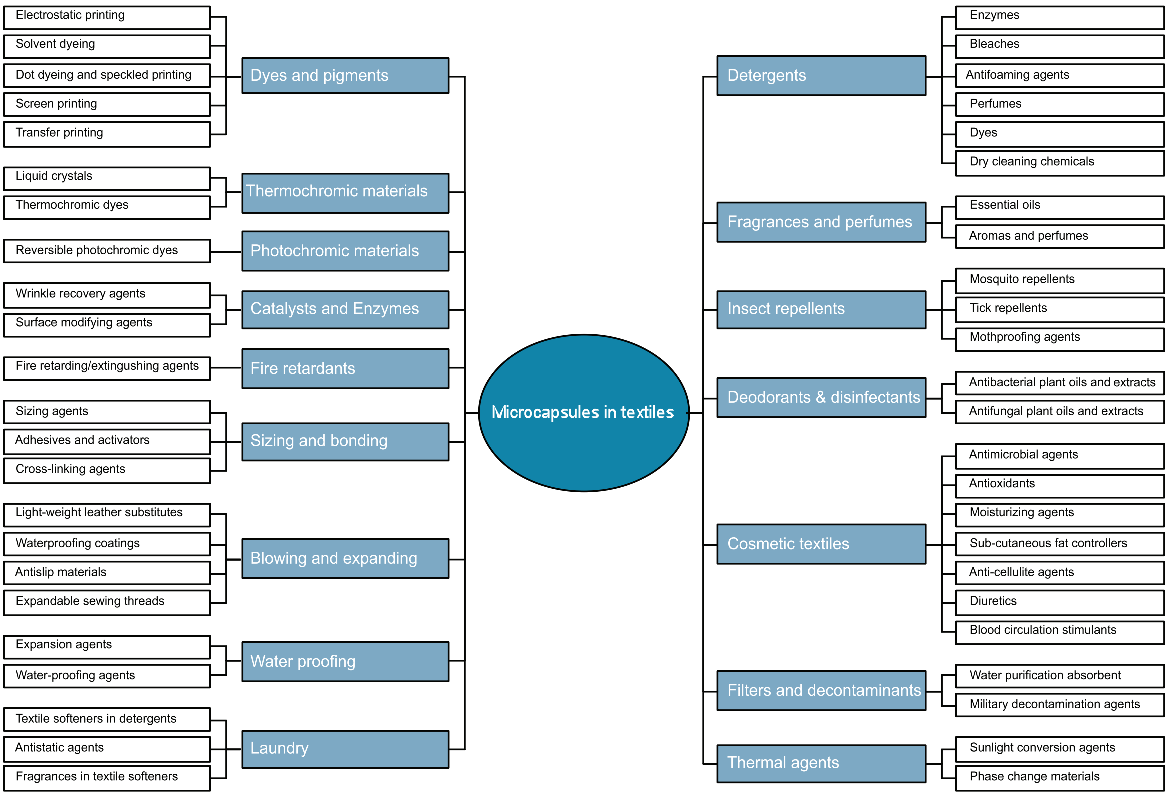


Figure 3: Applications of microcapsules in textile products (analysis and structuring of data from patents and scientific publications, CAPlus database search)

ture. 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. The transition process is completely reversible. To overcome practical problems of solid-liquid phase, PCMs have to be microencapsulated and turned into solid formulations for the use in various thermal management applications. Typical organic PCMs are higher hydrocarbons – paraffins and their narrow fractions – which are chemically inert, non-corrosive, long-lasting, inexpensive, ecologically harmless and non-toxic.

1.2 Microencapsulation processes

The choice of the microencapsulation process for textile applications depends on the desired characteristics and uses of the textile product. For example, microcapsule size, shape, wall material, active substance, release mechanism, method of application, and compatibility with the formulation of additives must be adapted to the requirements of textile processing methods and uses of the final product. Most often, microcapsules are prepared with one of the following three technological possibilities [7, 8]:

- *mechanical methods (e.g. spray drying, pan coating, extrusion, deposition in vacuum, solvent evaporation from emulsions) where the microcapsule wall is mechanically applied or condensed around the microcapsule core;*
- *coacervation, a phenomenon taking place in colloid systems where macromolecular colloid rich coacervate droplets surround dispersed microcapsule cores and form a viscous microcapsule wall, which is solidified with cross-linking agents (cf. Figure 4), and*
- *polymerisation methods where monomers polymerise around the droplets of an emulsion and form a solid polymeric wall. In the in situ polymerisation, monomers or precondensates are added only to the aqueous phase of emulsion (cf. Figure 5), while in interfacial polymerisation, one of the monomers is dissolved in the aqueous phase and the other in a lypophilic solvent.*

gorenja ter posebne funkcionalne tekstilije z mikrokapsuliranimi odvračali insektov, s protimikrobno zaščito, razkužili in deodoranti, bioaktivne medicinske in kozmetične tekstilije ter tekstilni izdelki z mikrokapsuliranimi fazno spremenljivimi materiali (Phase Change Materials – PCM) za aktivno toplotno upravljanje.

Najhitreje rastoča uporaba tehnologije mikrokapsuliranja na tekstilnem področju v zadnjem desetletju je za športna in posebna tehnična oblačila, ki temeljijo na mikrokapsuliranih PCM-jih z zmožnostjo absorpcije/oddajanja toplote (slika 1). Več podjetij tekmuje za pravice intelektualne lastnine ter tržne deleže na tem področju. Športne trgovine ponujajo plašče, jakne, škornje, nogavice in rokavice s termalno aktivno tehnologijo nadzora.

PCM-ji so podskupina materialov za shranjevanje toplote (Heat Storage Materials – HSM) za dinamično izmenjavo toplote pri temperaturi tališča PCM. Ob spremembi agregatnega stanja PCM-ja iz trdnega v tekoče se energija shrani v obliki latentne toplote pri konstantni temperaturi. Akumulirana toplotna energija se nato sprosti, ko se tekoči PCM znova strdi. Proces prehodov je popolnoma reverzibilen. Težave zaradi sprememb agregatnega stanja trdno-tekoče-trdno v praksi premagujemo z uporabo tehnologije mikrokapsuliranja, ki mikrokapsuliranim PCM zagotovi lastnosti trdnih snovi in s tem poveča možnosti za uporabo v različnih sistemih za upravljanje toplote. Značilni primeri organskih PCM so višji ogljikovodiki – ozke frakcije parafinov, ki so kemično inertni in nekorozivni, primerni za dolgotrajno uporabo, poceni, ekološko neškodljivi in nestrupeni.

1.2 Postopki mikrokapsuliranja

Izbira postopkov mikrokapsuliranja je odvisna od želenih lastnosti končnega tekstilnega izdelka. Velikost, oblika, material za ovojnico, aktivna substanca, mehanizem sproščanja, metode aplikacije in kompatibilnost z aditivi so lastnosti, ki jih je treba upoštevati pri načrtovanju tekstilnega postopka za izdelavo končnega izdelka. Najpogosteje so za mikrokapsuliranje uporabljeni postopki iz ene od naslednjih skupin [7, 8]:

- **Mehanski**, pri katerih steno mikrokapsul mehansko nanesemo ali kondenziramo okoli jedra mikrokapsul (npr. sušenje z razprševanjem, ekstrudiranje, napr̆ševanje v vakuumu, izparevanje topila iz emulzije ipd.).
- **Koacervacijski**, ki poteka v koloidnih sistemih, kjer makromolekularna koloidno bogata faza obda emulgirana jedra bodočih mikrokapsul in ustvari viskozno ovojnico, ki jo v nadaljevanju utrdimo z zamreževanjem (slika 4).
- **Polimerizacijski**, kjer monomeri polimerizirajo okoli kapljic v emulziji in stvorijo trdno polimerno steno. V postopkih *in situ polimerizacije* so monomeri ali prekondenzati dodani le v vodno fazo emulzije (slika 5), medtem ko je pri *medfazni polimerizaciji* eden od monomerov raztopljen v vodni fazi, drugi pa v lipofilnem topilu.

Microcapsules in water dispersions for textile finishing have to be resistant to mechanical and thermal stress. The microcapsule walls have to withstand the pressure of rollers and elevated temperatures when passing through the drying channels.

In the past, the preparation of durable microcapsules for textile finishing compositions was first based on coacervation (e. g. gelatin-gum arabic microcapsule walls), and later on polymerisation methods such as interfacial polycondensation (polyamide, polyester, polyurethane walls) and in situ polycondensation (aminoaldehyde resin walls). When the microcapsules are designed to release their content during textile dyeing, washing or drying, the walls must be water soluble or heat sensitive to dissolve or melt at a desired temperature. In such cases, physical (mechanical) microencapsulation methods are often used, especially fluidised bed, spray drying and spray cooling.

When the microcapsules with impermeable and pressure-sensitive walls are needed for technical applications, the in situ polymerisation of aminoaldehyde polymers continues to be the microencapsulation process of choice [9, 10, 11, 12, 13, 14]. In the microencapsulation by the in situ polymerisation of amino-aldehyde resins [5], hydrophobic core materials are emulsified in water, and all wall material components, dissolved in the continuous (aqueous) phase, react and distribute evenly over the surfaces of droplets in the emulsion. After the microencapsulation, formaldehyde residues can be removed from the suspension of microcapsules with the addition of scavengers, e.g. ammonium chloride [15] or ammonia.

Due to formaldehyde negative effects on health, Japan became the first country to introduce formaldehyde limits for textiles in 1973. The Law No. 112 (Control of Household Products Containing Harmful Substances), issued in 1974, set the maximum limit values for five substances, among them also for formaldehyde [16]. Moreover, in Europe, the legislation [17] regarding ECO is getting increasingly important. Directives are restricting the use of hazardous substances (Directives 76/769/EEC17, Annex to 76/769/EEC restrict the use of tris (2,3 dibromopropyl) phosphate, tris-(aziridinyl)-phos-

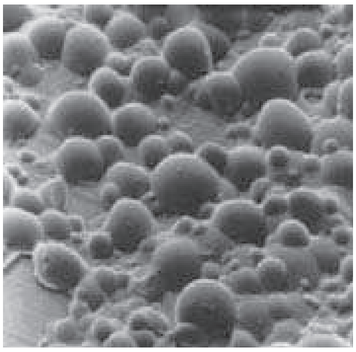


Figure 4: Coating of microcapsules, produced by complex coacervation of gelatin and carboxymethyl cellulose (SEM, 630×) with softer, elastic microcapsule walls

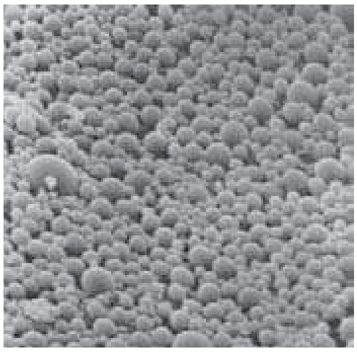


Figure 5: Coating of microcapsules, produced by in situ polymerisation of aminoaldehyde precondensates (SEM, 1900×) with impermeable, hard walls, which are pressure-sensitive

Mikrokapsule v vodni disperziji za plemenitenje tekstilnih izdelkov morajo biti odporne na mehanske in toplotne obremenitve; stene mikrokapsul morajo vzdržati pritisk valjev pri prehodu skozi sušilne poti.

V preteklosti je priprava trajnih mikrokapsul za tekstilno plemenitenje temeljila na postopku koacervacije (npr. želatina in gumi arabika za stene mikrokapsul), pozneje na postopku polimerizacije, kot medfazna polikondenzacija (poliamid, poliester, poliuretanske stene) ter na postopku *in-situ* polimerizacije (aminoaldehidne smole za stene). Če so mikrokapsule načrtovane za sprostitev vsebine v postopkih barvanja, pranja in sušenja tekstila, morajo biti stene topne v vodi ali občutljive na toploto, da se raztapljajo ali talijo pri želeni temperaturi. V takšnih primerih pogosto uporabljajo fizikalne (mehanske) metode mikrokapsuliranja, pogosto se uporablja še sušenje z razprševanjem ali hlajenjem.

Ko nastane potreba po mikrokapsulah z neprepustno ali na pritisk občutljivo steno, je postopek *in situ* polimerizacije aminoaldehidnih polimerov najboljša izbira [9, 10, 11, 12, 13, 14]. V postopku mikrokapsuliranja s polimerizacijo *in situ* aminoaldehidnih smol vstopajo vsi materiali za stene mikrokapsul iz kontinuirane vodne faze in se enakomerno razporejajo po površini kapljic v emulziji. Po mikrokapsuliranju lahko ostanke formaldehida odstranimo iz suspenzije mikrokapsul z dodajanjem posebnih lovilcev, kot je amonijev klorid [15] ali amoniak.

Zaradi negativnih učinkov formaldehida na zdravje je Japonska leta 1973 kot prva država uvedla omejitev količine formaldehida v tekstilu. V zakonu št. 112 (Nadzor nad izdelki za dom in gospodinjstvo, ki vsebujejo škodljive snovi), izdanem leta 1974, je predpisala najvišje dopustne koncentracije za pet spojin, med njimi tudi za formaldehid [16]. Tudi v Evropi je zakonodaja [17] v zvezi s standardi ECO čedalje pomembnejša. Direktive omejujejo *phinoxide, polybrominatedbiphenyls (PBB), pentabromodiphenyl ether (pentaBDE) andoctabromodiphenyl ether (octaBDE) in fireproofing garments. This, together with other legislation presented below, restricts the potentially hazardous substances which may be found in textile products. The new European Chemicals regulation REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) was adopted in December 2006. REACH Regulation (EC) No 1907/2006 and Directive 2006/121/EC amending Directive 67/548/EEC were published in the Official Journal on 30 December 2006. The emission of formaldehyde from the finished textile must not exceed 20 mg/kg for textiles for children in direct skin contact (< 24 months), 100 mg/kg for textiles in direct skin contact and 300 mg/kg for other textiles. These regulations place requirements on the fibre production, and the manufacturing process of textiles and garments as whole. Accordingly, aminoaldehyde microcapsule suspensions for textile applications have to be additionally processed for the removal of residual formaldehyde.*

Verifying the environmental and health parameters of textile products represents a significant challenge for public authorities. This is particularly difficult for the criteria referring to the production processes where compliance cannot be judged by testing the final product itself. Furthermore, non-experts cannot understand the complexity of the chemical information to be assessed. In some cases, the use of certain chemicals in the production process can to some extent be traced by assessing the final product, as residues remain.

1.3 Scanning electron microscopy for visualisation and characterisation of microcapsules

The morphology of microcapsules was analysed using SEM (Scanning electron microscopy) in previous works, e.g. by Su et al [18], where SEM was applied to study the structure and properties of microcapsules. SEM used in the research by Thrishna et al [19] revealed that the microcapsules were spherical with a nearly smooth surface. The characterisation of microcapsule properties, after the removal of excess formal-

uporabo nevarnih snovi (direktiva 76/769/EEC17: Priloga k direktivi 76/769/EGS, na primer, omejuje uporabo za tris (2,3 dibromopropil) fosfat, tris-(aziridinil)-fosfinoksid, polibromirane bifenile (PBB), pentabromodifenil eter (pentaBDE), andoctabromodifenil eter (oktaBDE)) v ognjevarnih oblačilih. Skupaj z drugo spodaj navedeno zakonodajo direktive omejujejo uporabo potencialno nevarnih snovi, ki jih lahko najdemo v tekstilnih izdelkih. Nova evropska uredba o kemikalijah REACH (registracija, evalvacija, avtorizacija in omejevanje kemikalij) je bila sprejeta decembra 2006. REACH Uredba (ES) št 1907/2006 in Direktiva 2006/121/ES o spremembi Direktive 67/548/EGS so bile objavljene v Uradnih listih z dne, 30. decembra 2006. Vsebnost formaldehida v končnih tekstilnih izdelkih ne sme presegati 20 mg/kg za tekstil za otroke v neposrednem stiku s kožo (<24 mesecev), 100 mg/kg za tekstil v neposrednem stiku s kožo ter 300 mg/kg za druge tekstilne izdelke. Ta pravilnik se nanaša na proizvodnjo vlaken, izdelavo tekstilij in oblačil kot celote. Zato je treba aminoaldehidne suspenzije mikrokapsul dodatno obdelati za tekstilno uporabo, ostanki formaldehida morajo biti odstranjeni.

Preverjanje okoljskih in zdravstvenih parametrov tekstilnih izdelkov je pomemben izziv za javne organe. To je še zlasti težko izvedljivo pri proizvodnih procesih, če skladnosti ni mogoče presojati s testiranjem končnega izdelka. Poleg tega ne-strokovnjaki težko razumejo kompleksnost kemijske informacije, ki jo je treba oceniti. V nekaterih primerih se uporaba nekaterih kemikalij v proizvodnem procesu lahko oceni tudi na končnem izdelku, ker sledovi ostanejo.

1.3 Vrstična elektronska mikroskopija za vizualizacijo in karakterizacijo mikrokapsul

Morfologija mikrokapsul je bila analizirana s pomočjo SEM (Scanning Electron Microscopy – vrstična elektronska mikroskopija). Su in sodelavci [18] so uporabili SEM mikroskopijo za študij strukture in lastnosti mikrokapsul. SEM je bila uporabljena tudi v raziskavah Thrishna in sodelavcev [19] – pokazala je, da so mikrokapsule okrogle s skoraj gladko površino. Značilne oblike mikrokapsul so po odstranitvi presežnega formaldehida z optično mikroskopijo in SEM vizualizirali Šumiga in sodelavci [20]. Elham in sodelavci [21] so proučevali površino mikrokapsul za določitev uporabe za tkanine. Analizirali so toplotno stabilnost med proizvodnim procesom. Morfologija nanokompozitnih mikrokapsul z vgrajenimi nanodelci ZnO je bila analizirana s konfokalno mikroskopijo, TEM, SEM in AFM pred in po obdelavi z ultrazvokom, avtorica Kolesnikova in sodelavci [22]. Opažena je bila izredno visoka občutljivost mikrokapsul na ultrazvok. Mehansko trdnost vključno s silo pretrga so proučevali Hu in sodelavci [23] za analizo uporabe mikrokapsul za funkcionalne samopopravljive materiale.

dehyde by ammonia, was visualised with optical and SEM microscopy by Sumiga et al [20]. The surface of microcapsules was studied to determine the application to fabrics by Elham et al [21] to observe the heat stability during the manufacturing process. The morphology of nanocomposite microcapsules with embedded ZnO nanoparticles was characterised with confocal microscopy, TEM, SEM and AFM before and after the ultrasound treatment by Kolesnikova et al [22], where a remarkably high capsule sensitivity to ultrasound was observed. The mechanical strength parameters including the rupture force was studied by Hu et al [23] to determine the use of microcapsules for the functional materials with self-healing properties.

The main purpose of our work was to present the possibilities of using SEM for the microencapsulation research purpose and for the visualisation of microcapsule applications on textiles. The synthesis of aminoplast microcapsules containing fragrances, essential oils and PCMs

2 Eksperimentalni del

Glavni namen našega dela dela je bil prikaz možnosti uporabe SEM v raziskavah mikrokapsuliranja ter za vizualizacijo mikrokapsul v tekstilnih aplikacijah. Sinteza mikrokapsul iz aminoplastov, ki vsebujejo dišave, eterična olja in PCM kot jedrni material, je prikazana na različnih tekstilnih aplikacijah. Poleg tega so nekatere lastnosti mikrokapsul vizualizirane z uporabo SEM, v kombinaciji s klasičnimi metodami analize mikrokapsul. Za statistično vrednotenje in grafični prikaz analize so posnetki SEM analizirani s programsko opremo ImageJ.

2.1 Sinteza aminoplastnih mikrokapsul

Mikrokapsule smo pripravili z modificirano metodo *in situ* polimerizacije [24, 25] aminoaldehidnih predpolimerov v 1-litrskem laboratorijskem reaktorju ter v 200-litrskem industrijskem reaktorju. Parafinski PCM (Rubitherm), eterična olj in dišave (Etol) so bili mikrokapsulirani za uporabo v tekstilstvu. Kot predpolimer za steno mikrokapsul smo uporabili metiliran trimetilolmelamin (Melamin). Kopolimer stirena in maleinanhidrida s povprečno molsko maso 350.000 g/mol (Hercules) je bil dodan kot emulgator in modifikator. Shematska slika procesa je na sliki 6.

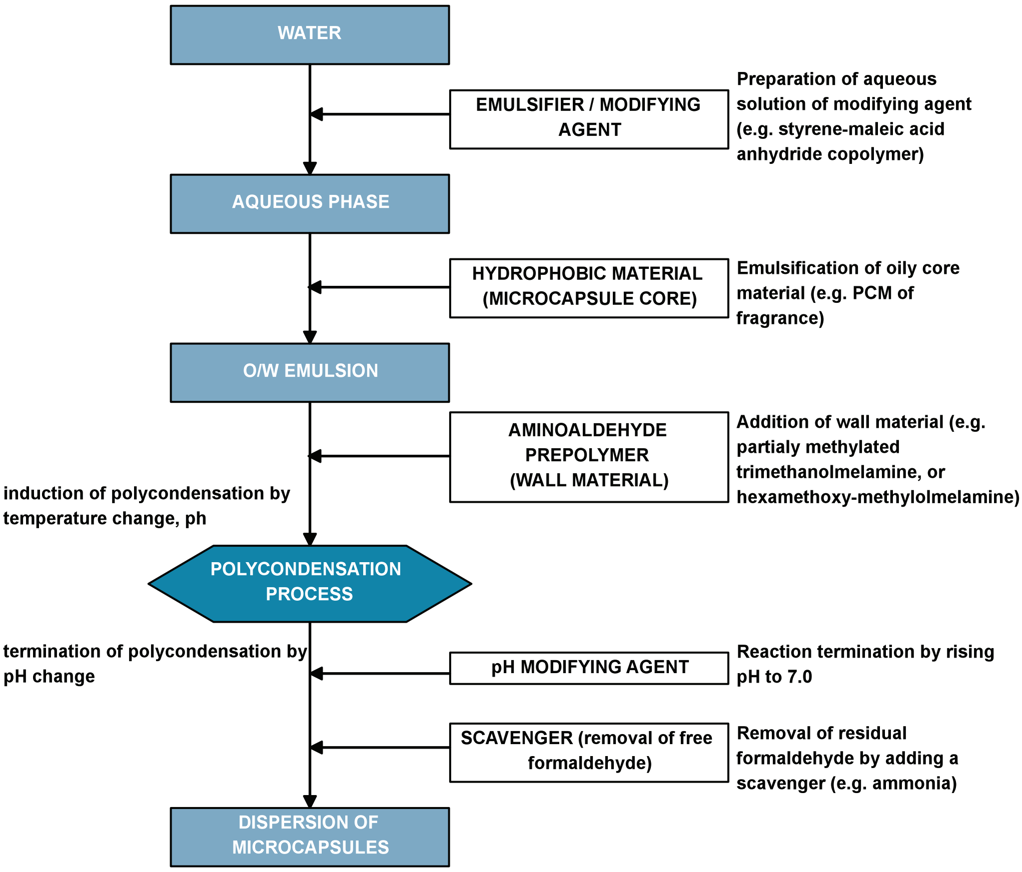


Figure 6: Synthesis of microcapsules by in situ polymerisation process

as core materials, in laboratory and semi-industrial reactors, and their applications to different textiles is described as well. In addition, some properties of microcapsules are visualised with the use of SEM, in combination with classical methods of microcapsule properties evaluation. For a statistical evaluation and graphical representation of analyses, the processing of SEM images was conducted with ImageJ software.

2 Experimental

2.1 Synthesis of aminoplast microcapsules

Microcapsules were prepared with a modified in situ polymerisation method [24, 25] of aminoaldehyde prepolymers (cf. Figure 6) in a 1 L laboratory reactor, and in 10 L and 200 L industrial stainless steel reactors. Paraffin phase change materials – PCM (Rubitherm), essential oils and fragrances (Etol) were microencapsulated for textile applications. As a prepolymer for the microcapsule wall, partly methylated trimethylolmelamine (Melamin) was used in the presence of an anionic emulsifier/modifying agent. A schematic representation of the synthesis process is presented in Figure 6.

2.2 Analysis and testing of microcapsules

The microcapsule diameter and size distribution were measured with an Alcatel Cilas Laser Granulometer 715. The pH values of microcapsule suspensions were determined with a laboratory pH meter with a glass electrode. The viscosities of suspensions were determined with a viscosity meter Anton Paar DV-1 P. The diffusion of core materials from dry microcapsules at an elevated temperature was measured in a ventilated oven as a mass loss at 135 °C, which corresponded to the temperature reached during the process of applying microcapsule suspensions to non-woven textile carriers. The mechanical strength of microcapsules was tested with a direct pressure mechanical strength test, based on a diffusion test [26] with a modification that samples were subjected to a direct force of different weights, in comparison with a sample without any force applied (cf. Figure 7). The pressure was generated by three standard-

2.2 Analiza in testiranje mikrokapsul

Premer in porazdelitev velikosti mikrokapsul so bili izmerjeni z uporabo Alcatel Cilas laserskega granulometra 715. pH suspenzije mikrokapsul smo določili v laboratoriju s pH-metrom s stekleno elektrodo. Viskoznosti suspenzij smo določili z aparaturo za analizo viskoznosti Anton Paar DV-1 P. Difuzija materialov iz jedra suhih mikrokapsul pri povišani temperaturi je bila izmerjena v ventilacijski peči kot izguba mase pri temperaturi 135 °C, kar je ustrezalo najvišji temperaturi v procesu impregnacije netkanih tekstilij z vodno suspenzijo mikrokapsul.

Mehansko trdnost mikrokapsul smo določali s testom direktnega mehanskega pritiska, na podlagi testa difuzije [26]. Vzorci so bili izpostavljeni različnim obremenitvam (slika 7). Pritisk so ustvarile standardne uteži (500 g, 1500 g, 3000 g) na površini 19,6 cm^2 vzorcev mikrokapsul z maso 3 g.

Morfologijo in povprečno velikost delcev mikrokapsul smo karakterizirali z uporabo JEOL JSM 6060LV mikroskopa (SEM).

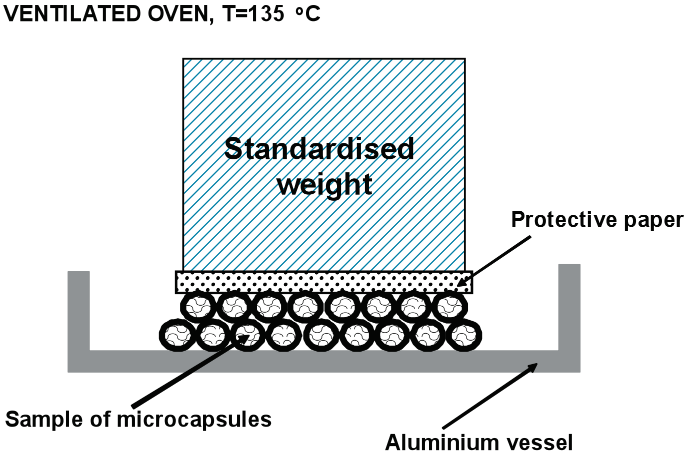


Figure 7: Direct pressure mechanical strength test of microcapsules in ventilated oven

2.3 Aplikacija mikrokapsul na tekstilne nosilce

Za uporabo mikrokapsul na tekstilnih izdelkih so bile uporabljene različne tehnike. V večini primerov so bile uporabljene vodne suspenzije mikrokapsul, nanesene na tekstilne nosilce z impregnacijsko tehniko, ki temelji na transportu tekstilnih nosilcev skozi impregnacijske bazene (slika 8) [27]. Na vzorcih na slikah 4 in 5 so bile mikrokapsule natisnjene s sitotiskom, na vzorcih na slikah 19 in 20 so bile nanesene s polindustrijskim premaznim strojem. Poliestrske, polipropilenske ter celulozno-polipropilenske netkane tekstilije (tipi 20, 30, 40, 45 g/m^2 in 250 g/m^2 za vložke za čevlje), so bile uporabljene kot tekstilni nosilci. Akrilni lateks je bil uporabljen kot vezivo v suspenziji mikrokapsul za tekstil. Vsi tekstilni vzorci so bili pridobljeni iz raziskovalno-razvojnega arhiva podjetja AERO.

ised weights (500 g, 1500 g, 3000 g) on a 19.6 cm^2 surface of 3 g microcapsule samples. The morphology and average particle size of microcapsules were characterised using a JEOL JSM 6060LV scanning electron microscope (SEM).

2.3 Application of microcapsules to textile carriers

For the application of microcapsules to textile carriers, different techniques were used. In most cases, aqueous microcapsule suspensions were applied with impregnation, using a technique based on the transport of the textile through the impregnation basin (cf. Figure 8) [27]. On the samples in Figures 4 and 5, the microcapsules were printed with screen printing, whereas on the samples in Figures 19 and 20, they were coated using a semi-industrial coating machine (Dixon). Polyester, polypropylene, and cellulose-polypropylene non-woven textiles (types of 20, 30, 40, 45 g/m^2, and 250 g/m^2 for shoe insoles) were used as textile carriers. Acrylic latex was used as the binder in microcapsule suspensions for textiles. All textile samples were acquired from the AERO R&D archives.

2.4 Visualisation and characterisation of microcapsules using SEM

Scanning electron microscopy (SEM) [28] was used for the visualising and studying of microcapsules in a suspension, after spray drying, or applied on textile carriers, as well as for the morphological characterisation and mechanical wall resistance of microcapsules in relation to the amount of ammonia used as a scavenger. The samples of microcapsules and textile carriers with microcapsules were coated with an ultra-thin coating of carbon, gold and platinum with high vacuum evaporation. The observations were performed with a JEOL JSM 6060LV SEM microscope at 10kV, which gave bright images of microcapsules [29]. With regard to the size of microcapsules, large magnifications up to 15,000× were required to observe the microcapsule wall thickness or for the effects of ammonia scavenger on the microcapsule morphology.

The SEM images were further analysed by the ImageJ [30] program, which is designed for the processing and analysis of images in various

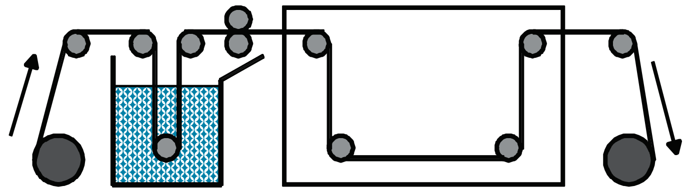


Figure 8: Impregnation of non-woven textile with aqueous formulation of microcapsules and binders: transport of textile carrier through impregnation basin, followed by drying

2.4. Vizualizacija in karakterizacija mikrokapsul z uporabo mikroskopije SEM

Vrstična elektronska mikroskopija (SEM) [28] je bila uporabljena za vizualizacijo in študij mikrokapsul na tekstilnih nosilcih, kot tudi za analizo morfoloških značilnosti in mehanske odpornosti stene mikrokapsul v odvisnosti od količine dodanega amoniaka kot odstranjevalca preostankov formaldehida. Vzorci mikrokapsul so bili naparjeni z ultra tanko plastjo ogljika, zlata in platine z visokovakuumskim naparevanjem. Raziskave so bile opravljene z mikroskopom SEM JEOL JSM 6060LV pri 10kV, ki je omogočil jasne posnetke mikrokapsul [15]. Glede na velikost mikrokapsul so bile za analizo debelosti sten mikrokapsul in za študij učinkov amoniaka na morfologijo sten mikrokapsul potrebne do 15.000-kratne povečave.

Mikrografije so bile dodatno analizirane z uporabo programa ImageJ, ki se uporablja za obdelavo in analizo podob v različnih formatih, deluje po spletu ali kot samostojna aplikacija. Program izračuna dimenzije, površine, statistično obdela slike ali podrobnosti, ki jih izbere uporabnik, kot so histogrami, profili, izmeri dimenzije, obvlada pa tudi standardne funkcije za obdelavo slik, kot so kontrast, ostrenje, glajenje, analiza robov, in tudi analizo barv.

3 Rezultati

3.1 Videz, morfologija, velikost mikrokapsul, debelina sten z analizo SEM

SEM je bila uporabljena za vizualizacijo in opredelitev površinske morfologije nastalih mikrokapsul. Primerjava fotografij mikrokapsul SEM s tremi različnimi jedrnimi materiali kaže gladko površino stene melamin-formaldehidnih mikrokapsul brez por, kar je značilno za *in situ* polimerizacijo v sistemu emulziji olje-v-vodi (slika 9).

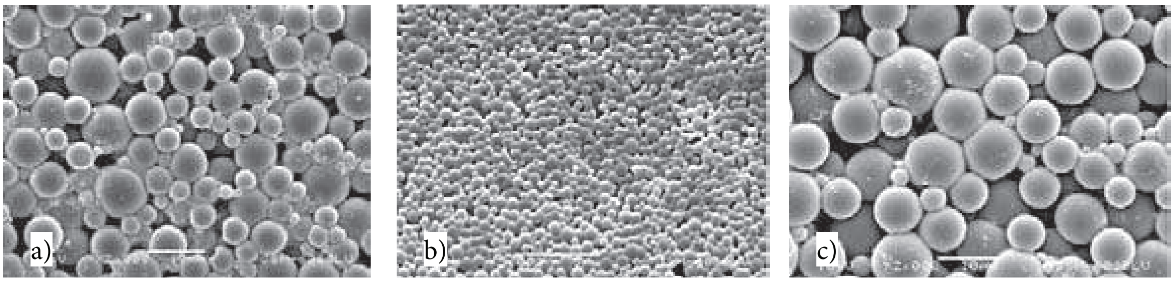


Figure 9: SEM photograph of microcapsules with rose fragrance (a) eucalyptus essential oil (b) and paraffinic PCM (c), SEM 2000×

formats, and can be used online or as a standalone application. The program calculates the area and pixel value statistics of user-defined selections, thus creating density histograms and line profile plots. The program enables the measuring of dimensions, as well as standard functions for image processing, e.g. contrast, sharpening, smoothing, analysis of the tunnel and colour analysis. It also supports standard image processing functions, e.g. contrast manipulation, sharpening, smoothing, edge detection and median filtering.

3 Results

3.1. Appearance, morphology, microcapsule size and wall thickness of microcapsules under SEM

SEM was applied to visualise and characterise the surface morphology of produced microcapsules. A comparison of SEM photographs of microcapsules with three different core materials revealed a smooth melamine-formaldehyde resin microcapsule wall surface without pores, which seems to be characteristic for the in situ polymerisation process in oil-in water emulsion systems (cf. Figure 9).

Furthermore, with the assumption that all wall material uniformly forms the walls around the microcapsule cores and that microcapsules are spheres with a diameter D, we can derive Equation 1 for the calculation of microcapsule wall thickness (Equation 1), where d – wall thickness, D – diameter of microcapsules, R – ratio of wall material to core material, ρ_j – density of core material and ρ_s – density of wall material.

In the chemical process of microencapsulation by the in situ polymerisation, the microcapsules

Ob predpostavki, da material za steno enakomerno obda jedra mikrokapsul in da so mikrokapsule okrogle oblike s premerom D, lahko razvijemo enačbo 1 za izračun debeline stene mikrokapsule, kjer je: d – debelina stene, D – premer mikrokapsule, R – razmerje materiala stena/jedro, ρ_j – gostota materiala jedra in ρ_s – gostota materiala stene.

$$d = \frac{D}{2} \times \left(1 - \sqrt[3]{\left(\frac{1}{1 + R \times \frac{\rho_j}{\rho_s}}\right)}\right) \qquad (1)$$

V postopku mikrokapsuliranja z *in situ* polimerizacijo so mikrokapsule v končni suspenziji različnih velikosti. Z rezultati meritev velikosti in volumna v %, opravljenimi z inštrumentom za merjenje velikosti delcev, je mogoče po enačbi 2 dobiti povprečno debelino stene izdelanih mikrokapsul, kjer je: $\bar{d}$ – povprečna debelina stene, w_i – delež mikrokapsul z izračunanim d_i iz analize velikosti delcev, in d_i – izračunan premer mikrokapsul z izbranim D iz analize velikosti delcev.

$$\bar{d} = \sum_{i=1}^{n} w_i \times d_i \qquad (2)$$

Izračunane vrednosti debeline stene mikrokapsul so bile primerjane z izmerjeno debelino stene s pomočjo SEM. Z uporabo enačbe 1 in povprečnih vrednosti premera mikrokapsul, dobljenih z lasersko granulometrijo, je bila predvidena vrednost debeline stene mikrokapsul 104 nm. Z dodatnim upoštevanjem enačbe 2 je bila izračunana predvidena debelina stene mikrokapsul 112 nm. Izračunane vrednosti so bile v skladu z dejanskimi meritvami debeline stene počenih mikrokapsul s SEM analizo (slika 10).

SEM posnetki so bili dodatno analizirani s programom ImageJ, da bi dobili povprečno velikost mikrokapsul. Te vrednosti smo primerjali z rezultati meritev velikosti mikrokapsul z lasersko granulometrijo (slika 11). Primerjava obeh rezultatov je pokazala, da je uporaba analize SEM mogoča tudi za določanje povprečnih vrednosti velikosti mikrokapsul.

in a resultant suspension of microcapsules are of different sizes. By using the results of microcapsule size measurements in volume % made with a particle size analyser, it is possible to obtain an average wall thickness of produced microcapsules by applying Equation 2, where $\bar{d}$ – average wall thickness, w_i – proportion of microcapsules with calculated d_i from the particle size analysis and d_i – a calculated diameter of microcapsules with a selected D from the particle size analysis.

The mathematically calculated values of the wall thickness were compared with the microcapsule wall thickness visualised by SEM. When using only Equation 1 and an average microcapsule diameter obtained with laser granulometry, the predicted microcapsule wall thickness was 104 nm. Additionally, by taking into account Equation 2, the calculated thickness of microcapsule walls was 112 nm. This was in accordance with the observed dimensions of the wall thickness in broken microcapsules on SEM images (cf. Figure 10).

In addition, the SEM image analysis with ImageJ software was applied to obtain the average microcapsule size on SEM photographs. These values were then compared with the particle size analyser measurements based on laser granulometry (cf. Figure 11). A comparison shows that it is possible to some extent to use SEM as the tool not only for the size determination of some microcapsules, but also for obtaining the average microcapsule size.

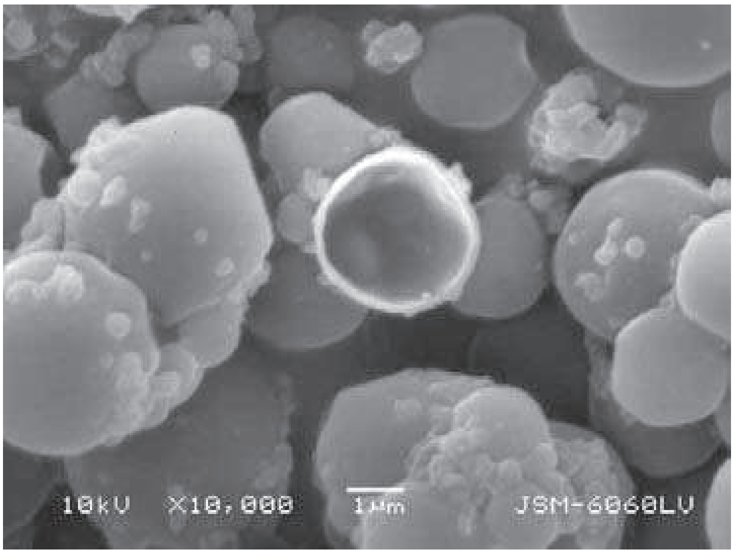


Figure 10: SEM visualisation of microcapsule wall thickness

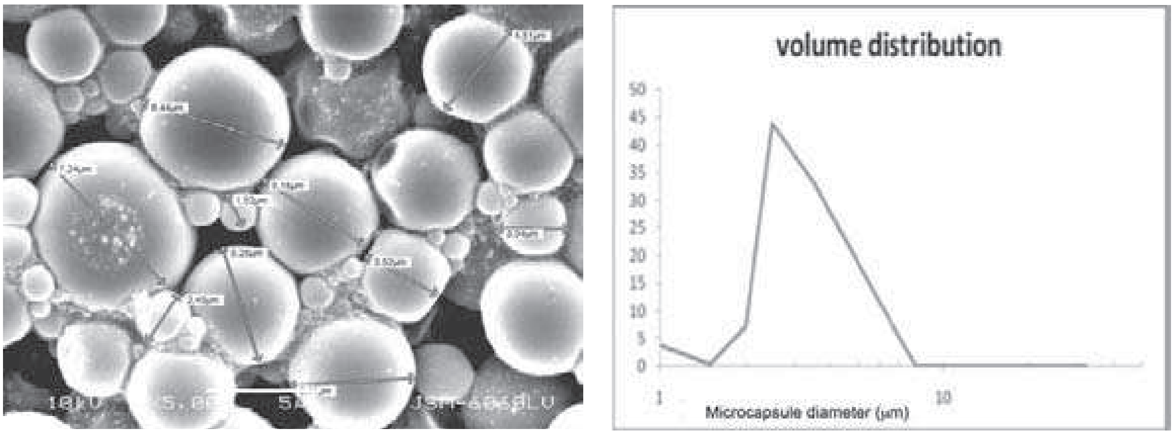


Figure 11: Microcapsule sizes obtained with SEM (left) and microcapsule size distribution obtained with laser granulometry (right)

3.2 Mikrokapsuliranje dišav in eteričnih olj ter vizualizacija mikrokapsul na tekstilnih izdelkih

Glavni parametri procesa *in situ* polimerizacije za mikrokapsuliranje dišav in eteričnih olj v 10-litrskem reaktorju so navedeni v tabeli 1. V tabeli 2 pa so prikazane lastnosti dobljenih mikrokapsul. Za analizo morfologije in distribucije mikrokapsul na tekstilnih izdelkih so bili uporabljeni posnetki SEM aminoaldehidnih mikrokapsul na tkanih in netkanih tekstilnih izdelkih pri 500-kratni in 2000-kratni povečavi (slike 12–20).

SEM posnetki na pritisk občutljivih mikrokapsuliranih dišav na dekorativnem ovojnem traku za darila se predstavljeni na sliki 12; dišava se sprosti zaradi mehanskega pritiska pri rokovanju.

Na sliki 13 so SEM posnetki suhega osvežilnega robčka z dolgotrajno učinkovitostjo, izdelanega iz sintetične netkane tekstilije, impregnirane z evkaliptovim eteričnim oljem v mikrokapsulah,

Table 1: Main parameters of in situ polymerisation process for microencapsulation of fragrances and essential oils

Parameter	Value
Stirring rate	1500/min
Heating/cooling rate	0–2 °C/min
Emulsification temperature	20–30 °C
Emulsification time	20 min
Polymerisation time	60–90 min
Polymerisation temperature	60–85 °C

Table 2: Properties of microcapsules containing fragrances and essential oils

Parameter	Value
Wall material	melamine-formaldehyde resin
Core material	synthetic fragrance or natural essential oil
pH	6–8.5
Viscosity	200–300 mPas
Microcapsule content in suspension	32–38%
Microcapsule sizes	1–10 µm
Microencapsulation efficiency	more than 95%

3. 2 Microencapsulation of fragrances and essential oils, and visualisation of microcapsules on textile carriers

The main parameters of the in situ polymerisation process for the microencapsulation of fragrances and essential oils in a 10 L reactor are listed in Table 1, and the properties of produced microcapsules in Table 2. In order to visualise the microcapsules, their morphology and distribution on textiles, SEM images of aminoaldehyde microcapsules on woven and non-woven textile products, were compared at magnifications 500× and 2000× (cf. Figures 12–20).

Some of the textiles from Aero R&D archives were produced more than 10 years ago. Their recent SEM analysis (cf. Figures 12–20) reveals that microcapsule walls produced by the in situ polymerisation of aminoaldehyde resins have

občutljivih na pritisk. Eterično olje je shranjeno v jedru mikrokapsule in zaščiteno pred oksidacijo, dokler stena mikrokapsule ne poči pod mehanskim pritiskom ob uporabi robčka.

Slika 14 predstavlja posnetke s SEM odišavljenih najlonskih nogavic z eteričnim oljem vrtnice v mikrokapsulah, občutljivih na pritisk.

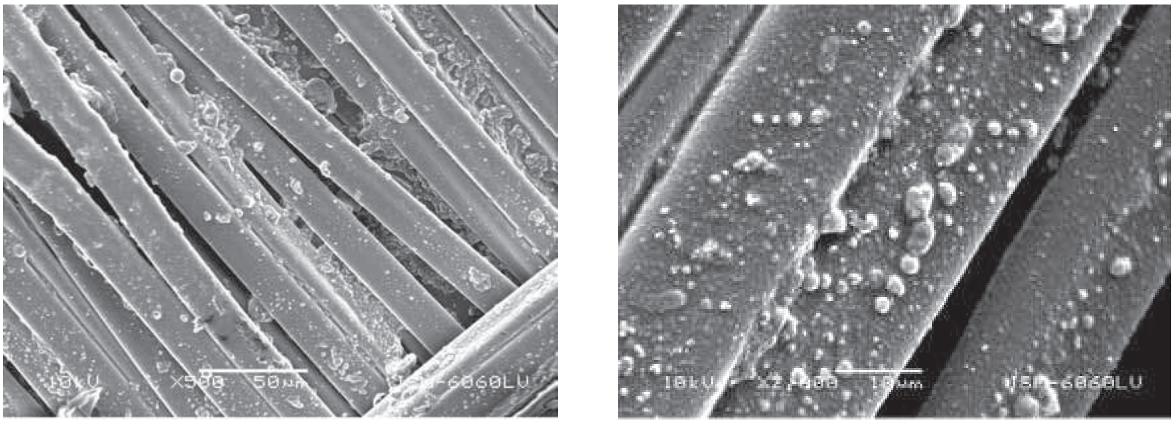
Zelena dekorativna tekstilija z dolgotrajnim vonjem smreke, predstavljena na sliki 15, je posneta s SEM; mikrokapsule so vključene v impregnacijsko zmes.

SEM posnetki rdeče dekorativne netkane tekstilije z dolgotrajnim vonjem jagode v mikrokapsulah, občutljivih na pritisk, so na sliki 16. Tkanina je primerna npr. za namizne prte.

Posnetki SEM na pritisk občutljivih mikrokapsul z aromo vanilije na rumeni netkani tekstiliji, primerni za dekoracijo in embalažo, so na sliki 17.

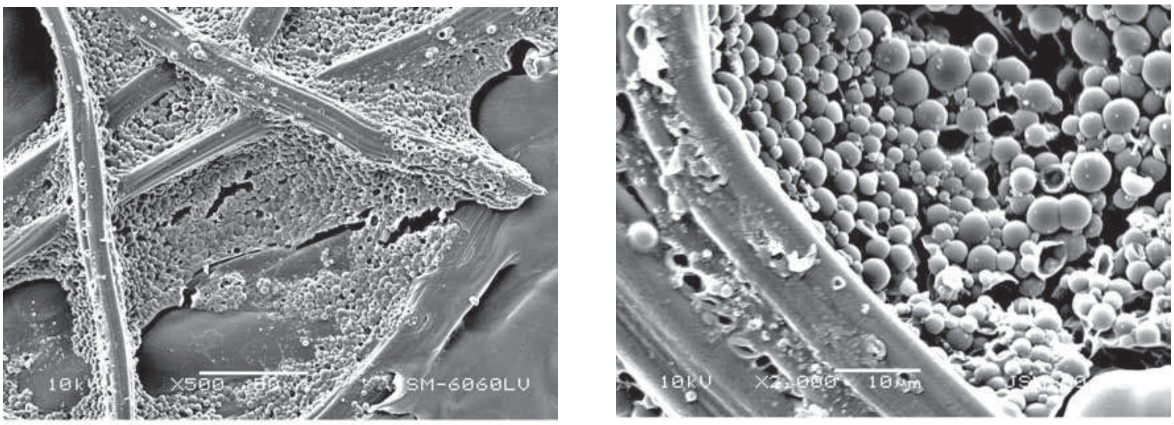
Na sliki 18 so predstavljeni SEM posnetki netkane tekstilije, impregnirane z mikrokapsulirano aromo kave, za uporabo v oglaševanju in zunanji embalaži živilskih izdelkov.

Slika 19 predstavlja SEM posnetek tekstilnega vložka za obutev



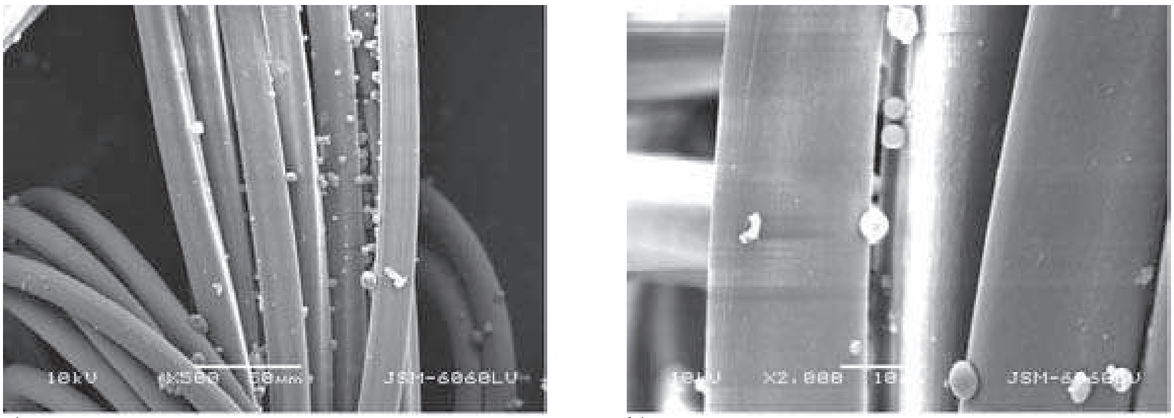
a) 500× b) 2000×

Figure 12: SEM of pressure-sensitive microencapsulated fragrances on decorative wrapping ribbon; fragrances are released by mechanical pressure applied by handling



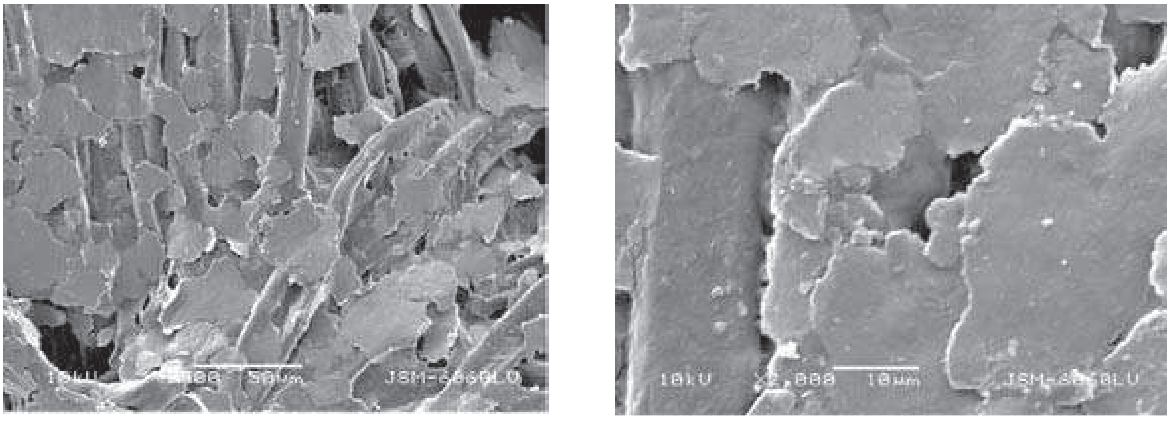
a) 500× b) 2000×

Figure 13: SEM of long-lasting dry refreshing handkerchief made of synthetic non-woven textile, impregnated with pressure-sensitive microencapsulated eucalyptus oil. Essential oil is preserved in the microcapsule core, protected from oxidation, until microcapsule wall bursts open by mechanical pressure when the handkerchief is used.



a) 500× b) 2000×

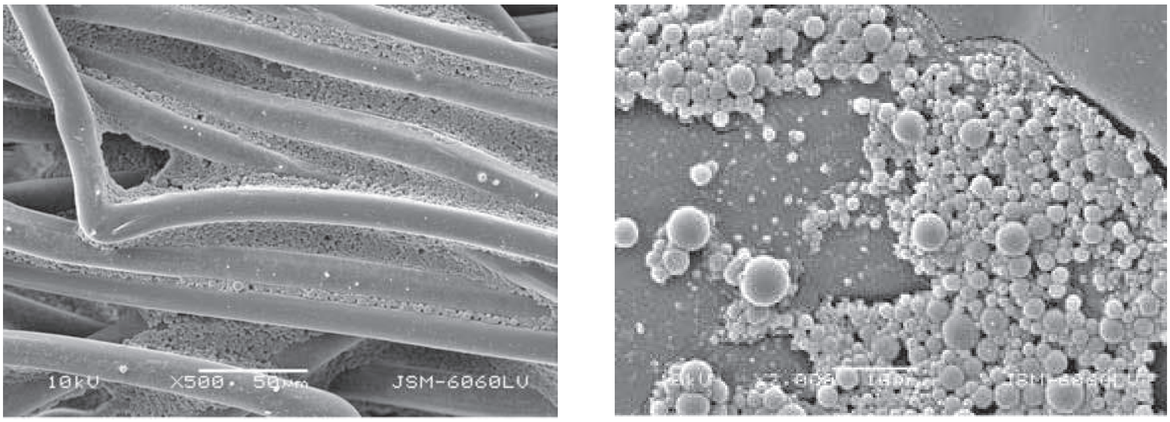
Figure 14: SEM of scented nylon pantyhose with microencapsulated rose oil in pressure-sensitive microcapsules



a) 500×

b) 2000×

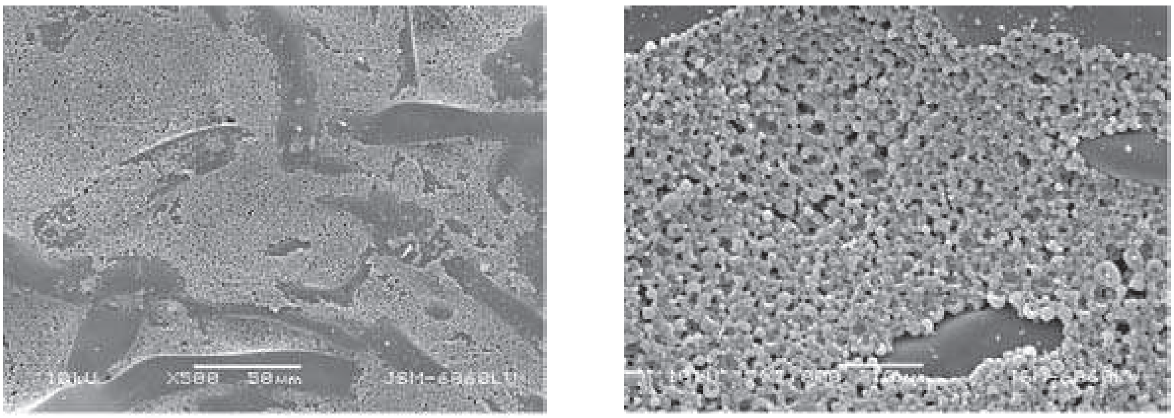
Figure 15: SEM of green decorative fabric with long lasting microencapsulated fragrance of spruce, incorporated in impregnation composition



a) 500×

b) 2000×

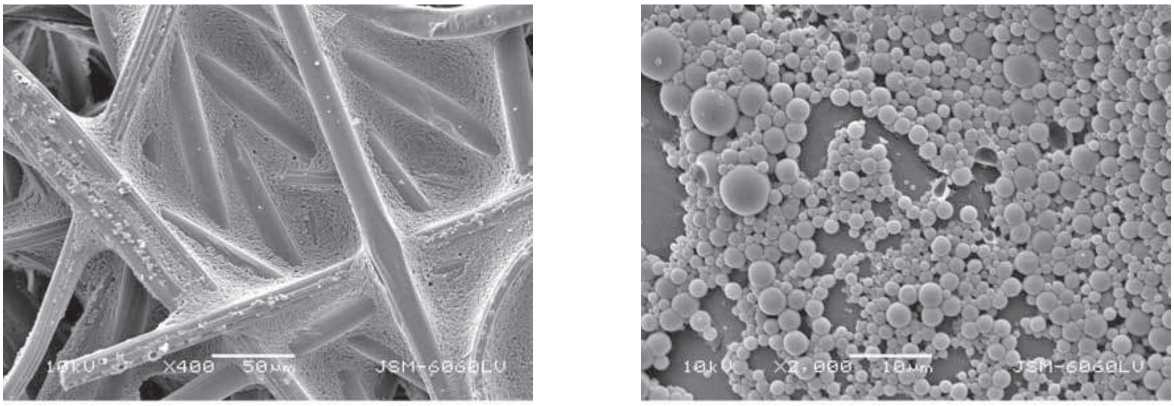
Figure 16: SEM of red non-woven decorative fabric with long-lasting fragrance of strawberry in pressure-sensitive microcapsules, applied e.g. for table cloth



a) 500×

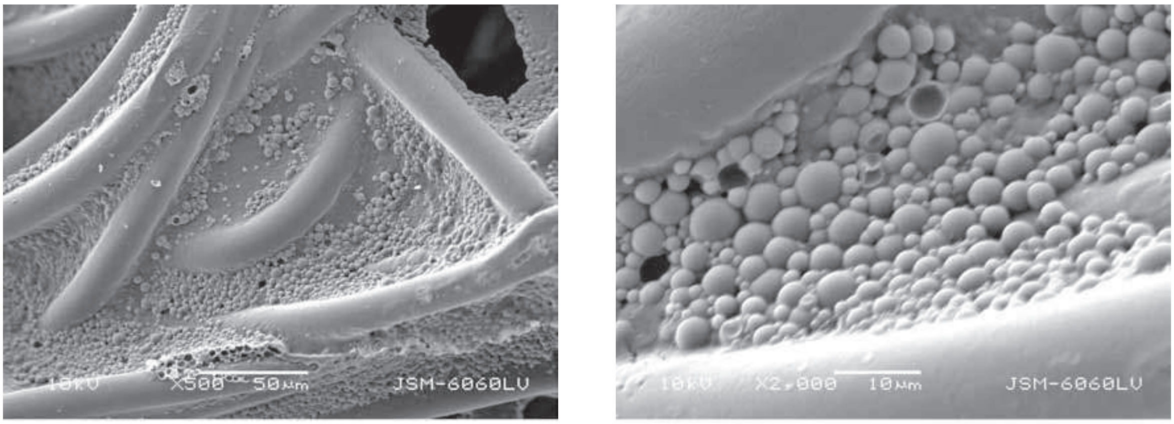
b) 2000×

Figure 17: SEM of long-lasting vanilla fragrance in pressure-sensitive microcapsules impregnated on yellow non-woven textile carrier, applicable for decoration and packaging



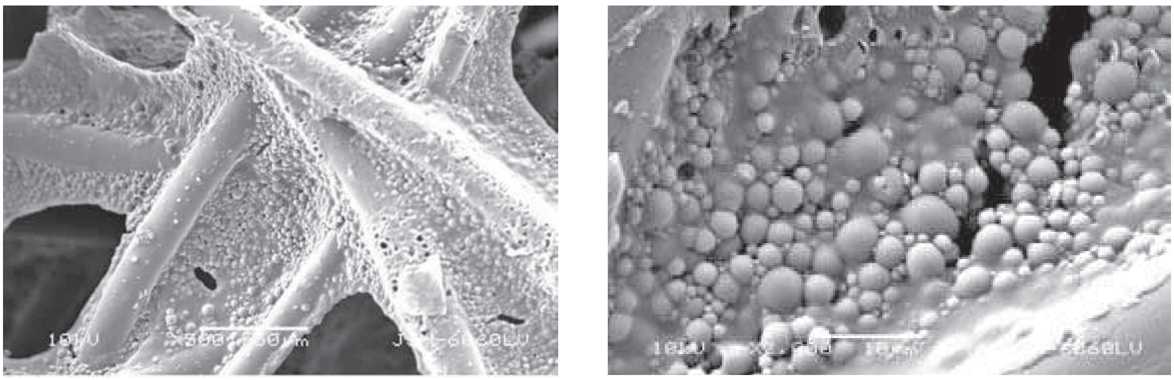
a) 400× b) 2000×

Figure 18: SEM of non-woven fabric impregnated with microencapsulated coffee fragrance, applicable for food advertising and packaging



a) 500× b) 2000×

Figure 19: SEM of textile shoe insole (Step on citrus): synthetic non-woven textile impregnated with long-lasting pressure-sensitive microcapsules, containing citrus oil as deodoriser, which is released during walking.



a) 500× b) 2000×

Figure 20: SEM of textile shoe insole (Nature): non-woven textile impregnated with pressure-sensitive microcapsules, containing composition of antimicrobial essential oils of lavender (Lavandula sp.), rosemary (Rosmarinus officinalis) and sage (Salvia officinalis). Essential oils are protected from oxidation until microcapsules are opened by mechanical pressure during walking and the antimicrobial compound is released.

been durable and stable for at least a decade. Additionally, the SEM visualisation confirmed that during the processes of applying microcapsules to textile carriers, the microcapsules had a sufficient mechanical and thermal resistance not to be damaged, broken or decomposed. After applying an external mechanical pressure, fragrances and essentials oils were released from the microcapsule core and produced a strong characteristic smell, even after a decade of storing the samples at a room temperature.

3.3 SEM as micro-level visualisation support in evaluation of mechanical resistance of PCM microcapsule walls

Impermeable walls with good mechanical resistance are particularly important in the microencapsulation of PCM, which should not fracture during the production and use of a product. Otherwise, by passing the phase change temperatures, PCM would drain away and the product would become useless.

The mechanical resistance of microcapsules was examined with a direct pressure mechanical strength test of microcapsules, by placing 500 g, 1500 g and 3000 g weights on a 19.6 cm² round surface of 3 g microcapsule samples in a layer, at an elevated temperature of 135 °C. At these conditions, the release of the core material was measured gravimetrically as the percentage of mass loss with time (cf. Figure 21). In all cases, the mass loss was below 2.5%, indicating a good mechanical resistance of melamine-formaldehyde polymeric walls to direct pressure. Slight differences were observed in release profiles. As expected, the mass loss increased at higher pressure. Microscopically, the differences in microcapsule wall damage were visualised with SEM (cf. Figure 22).

3.4 SEM for detecting morphological changes of PCM microcapsules caused by ammonia scavenger

The main process parameters and properties of PCM microcapsules produced by the in situ polymerisation in a 200 L industrial reactor, using ammonia for the removal of residual formaldehyde, are listed in Tables 3–4.

SEM was applied to detect potential morpho-

(*Step on citrus*): sintetična netkana tekstilija je impregnirana z dolgotrajno dišečimi in na pritisk občutljivimi mikrokapsulami, ki kot deodorant vsebujejo eterično olje citrone. Sprošča se pod pritiskom med hojo.

Na sliki 20 je prikazan SEM posnetek tekstilnega vložka za obutev (*Nature*): sintetična netkana tekstilija je impregnirana z na pritisk občutljivimi mikrokapsulami, ki vsebujejo zmes eteričnih olj s protimikrobnimi učinki (sivka *Lavandula sp.*, rožmarin *Rosmarinus officinalis* in žajbelj *Salvia officinalis*). Eterična olja so zaščitena pred oksidacijo, dokler se pod pritiskom ob hoji mikrokapsule postopoma ne odprejo in sprostijo aktivno učinkovino.

Nekatere tekstilije iz raziskovalno-razvojnega Aero, d. d. so bile pripravljene pred več kot 10 leti. SEM analize vzorcev (slike 12–20) razkrivajo, da so stene mikrokapsul, izdelane z *in situ* polimerizacijo aminoaldehidnih smol, trpežne in stabilne najmanj deset let. Poleg tega je SEM vizualizacija potrdila, da so med postopki nanašanja mikrokapsul na tekstilne nosilce le-te imele zadostno mehansko in toplotno odpornost, saj ni bilo opazno poškodovanih, zdrobljenih ali razgrajenih mikrokapsul. Pri uporabi z zunanjim mehanskim pritiskom so se dišave in eterična olja sproščala iz jedra mikrokapsul in proizvajala močan značilen vonj, celo po desetletju hranjenja vzorcev na sobni temperaturi.

3.3 SEM kot podpora vizualizacije na mikroravni za oceno mehanske odpornosti sten mikrokapsul

Neprepustne stene mikrokapsul z dobro mehansko odpornostjo so pomembne zlasti pri mikrokapsuliranih PCM, da ne bi prišlo do poškodb mikrokapsul med proizvodnjo ali uporabo v celotnem obdobju uporabnosti izdelka. V nasprotnem primeru bi PCM pri temperaturi faznega prehoda odtekli iz mikrokapsul in izdelek bi postal neuporaben.

Mehanska odpornost mikrokapsul je bila testirana na podlagi neposrednega pritiska različnih uteži (500 g, 1500 g, 3000 g), ki smo jih položili na okroglo površino 19,6 cm² vzorcev mikrokapsul z maso 3 g pri povišani temperaturi 135 °C.

V teh razmerah je bila sprostitev jedra gravimetrično merjena kot odstotek izgube mase s časom (slika 21). V vseh primerih je bila izguba mase manjša od 2,5 %, kar kaže na dobro odpornost melamin-formaldehidnih sten na neposreden mehanski pritisk. V profilih sproščanja so opazne manjše razlike, kot je bilo pričakovano; izguba mase jedra je bila povečana pri večjem pritisku. Mikroskopsko so bile spremembe in poškodbe na stenah mikrokapsul vizualizirane tudi s SEM (slika 22).

logical changes of microcapsules after the removal of residual formaldehyde from microcapsule aqueous suspensions with ammonia scavenger. Comparisons of SEM images taken with microcapsules, treated with different ammonia concentrations suggested that ammonia scavenger affected microcapsule wall characteristics (cf. Figures 23 a–28 a). Microcapsules with no ammonia scavenger tended to have more brittle and pressure-sensitive walls, which were prone to cracking, while by increased the concentrations of ammonia, microcapsules tended to have more elastic/durable walls.

The ImageJ analysis [30] (Figures 23 b, c–28 b, c) was used to additionally analyse SEM photographs. To observe the noticeable differences between microcapsules, samples were analysed and compared at 5,000×, 10,000× and 15,000× magnification. The ImageJ analysis plot profiles were more irregular in the case of samples with no ammonia added. The addition of ammonia resulted in profiles with higher regularity, indicating that the microcapsules were more uniform, with less broken spheres. In 3D surface plots, all these observations were even more evident.

The ImageJ analysis of samples suggested that the microcapsules with 1.35% added ammonia were more uniform, spherical, with fewer damaged/irregular capsules. The samples with no added ammonia were more diverse, with larger differences between the spherical/whole and

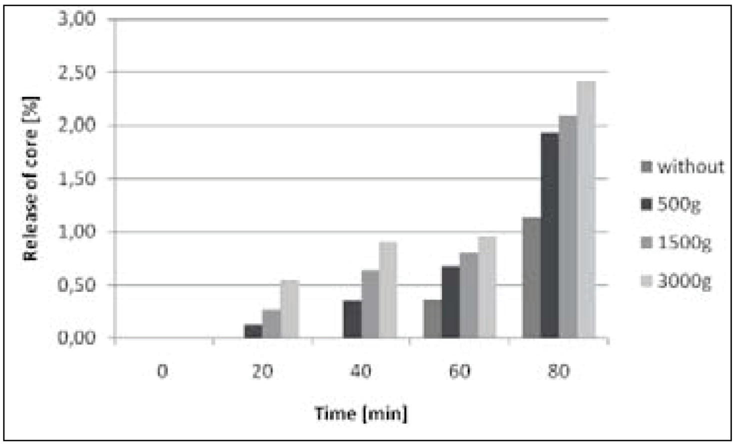
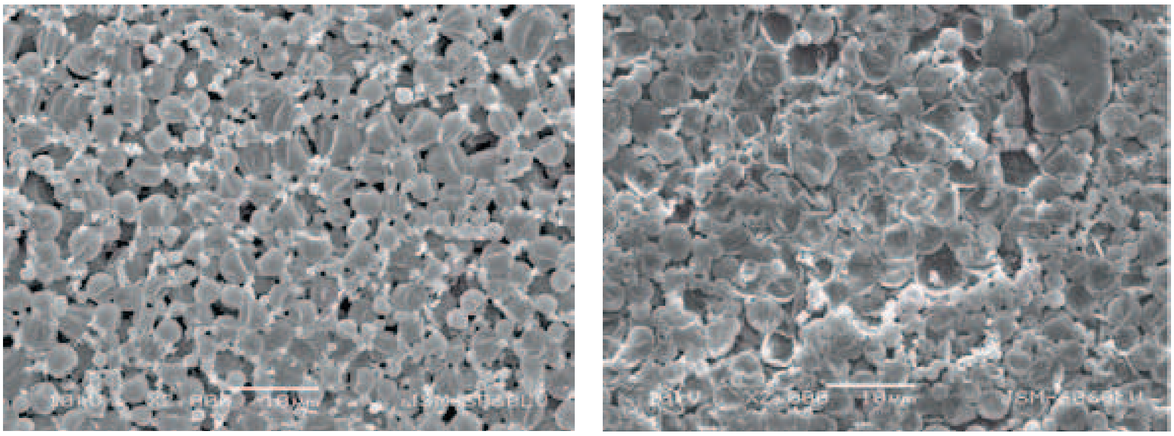


Figure 21: Release of microcapsule core material under 500 g, 1500 g, and 3000 g weights, compared to control (no weight) at elevated temperature of 135 °C



a) 2000× b) 2000×

Figure 22: SEM visualisation of microcapsules with no weight and after exposure to direct pressure of 3000 g weight in ventilated oven at 135 °C

3.4 SEM za odkrivanje morfoloških sprememb mikrokapsul po dodajanju amoniaka kot lovilca ostankov formaldehida

Glavni procesni parametri ter lastnosti mikrokapsul, pridobljenih z *in situ* polimerizacijo v 200-litrskem polindustrijskem reaktorju, z uporabo amoniaka kot lovilca za odstranitev preostalega formaldehida, so navedeni v tabelah 3 in 4.

Posnetki SEM so bili uporabljeni za ugotavljanje morebitnih morfoloških sprememb mikrokapsul po odstranitvi ostankov formaldehida iz vodne suspenzije mikrokapsul z amoniakom kot lovilcem. Primerjave SEM-posnetkov mikrokapsul z različnimi koncentracijami amoniaka kot lovilca formaldehida so nakazale, da je amoniak vplival na lastnosti sten mikrokapsul (slike 23 a–28 a). SEM-posnetki mikrokapsul brez dodanega amoniaka za odstranjevanje formaldehida so nakazovali bolj krhke in na pritisk občutljive stene mikrokapsul, z večjim številom poškodb, med-

Table 3: Main process parameters of in situ microencapsulation in 200 l reactor

Parameter	Value
Stirring rate	1500 rpm
Heating/cooling rate	0–2 °C/min
Emulsification temperature	25–40 °C
Emulsification time	30 min
Polymerisation time	60 min
Polymerisation temperature	60–85 °C

Table 4: Properties of PCM microcapsules produced in 200 l reactor

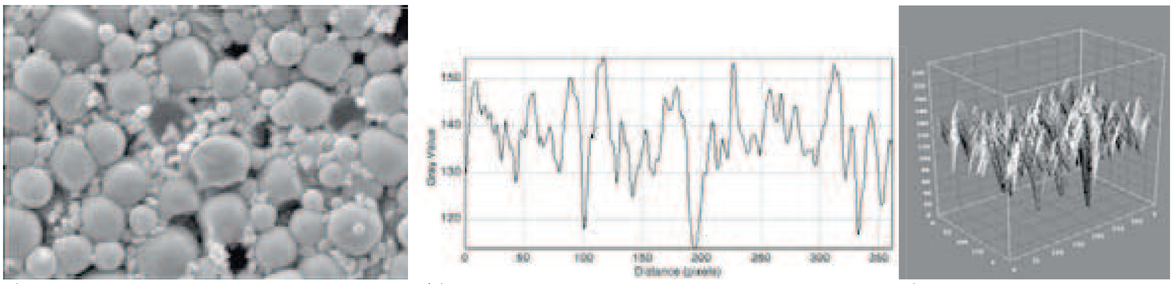
Parameter	Value
Wall material	melamine-formaldehyde resin
Core material	paraffinic PCM
pH	6–8.5
Viscosity	300–800 mPas
Microcapsules content in suspension	30–35%
Microcapsule sizes	1–10 µm
Microencapsulation efficiency	more than 95%

damaged capsules. Noteworthy were the injured, i.e., capsules. In the determination of microcapsule morphology, all the presented analyses were useful, all suggesting that the use of ammonia resulted in better, stronger microcapsules.

To confirm the observations obtained with a SEM morphological characterisation of PCM microcapsules, additional tests were performed with gravimetry, i.e. mass loss measurements, at an elevated temperature of 135 °C. The PCM mass loss measurements confirmed a positive

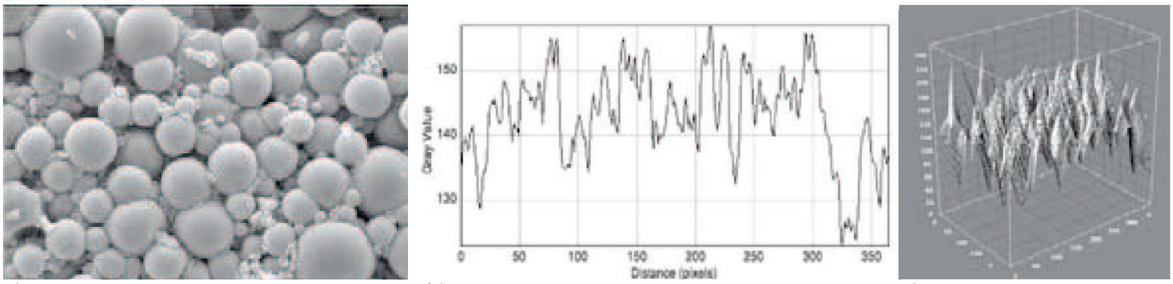
tem ko so bile mikrokapsule s povečano koncentracijo amoniaka na posnetkih večinoma vidne kot bolj elastične in odporne.

Analiza ImageJ [30], (slike 23 b, c–28 b, c) je bila uporabljena za dodatno analizo SEM fotografij. Za oceno opaznih razlik med mikrokapsulami so bili vzorci analizirani in primerjani pri 5000-kratni, 10.000-kratni in 15.000-kratni povečavi. Analiza ImageJ s ploskovnim profilom je pokazala več nepravilnosti pri vzorcih brez amoniaka. V primeru dodatka amoniaka je bil opazen boljši profil, ki je kazal bolj enotne in manj poškodovane mikrokapsule. Pri 3D analizi površine so bile vse te razlike še bolj očitne.



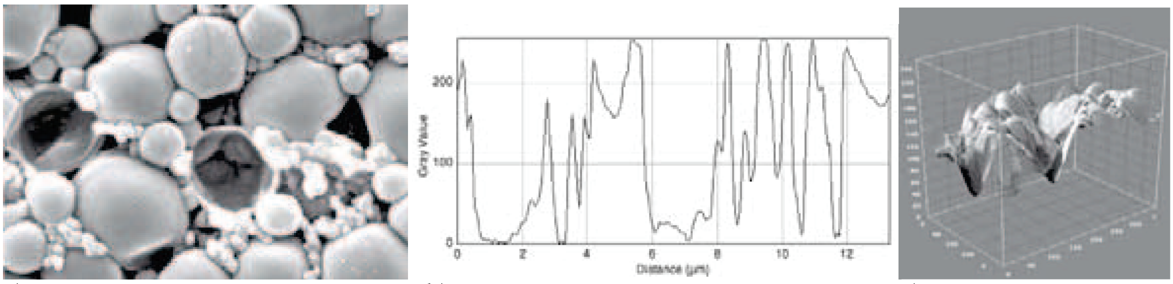
a) b) c)

Figure 23: a) SEM image of microcapsules with no ammonia added (5,000×), b) ImageJ analysis profile, c) Interactive 3D surface plot



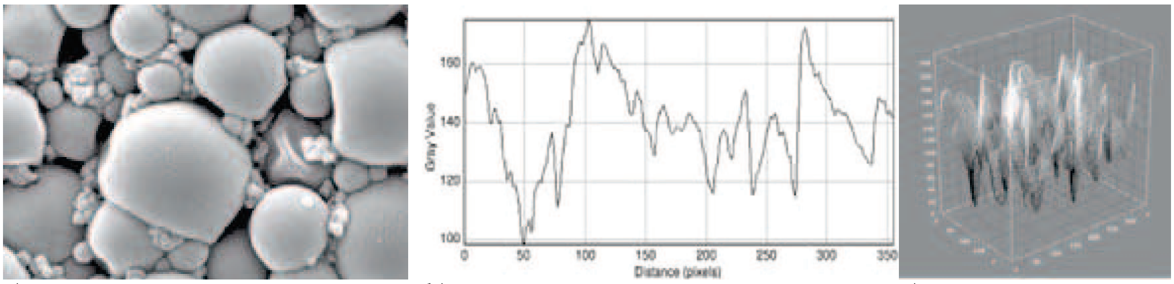
a) b) c)

Figure 24: a) SEM image of microcapsules with 1.35% ammonia added (5,000×), b) ImageJ analysis profile, c) Interactive 3D surface plot



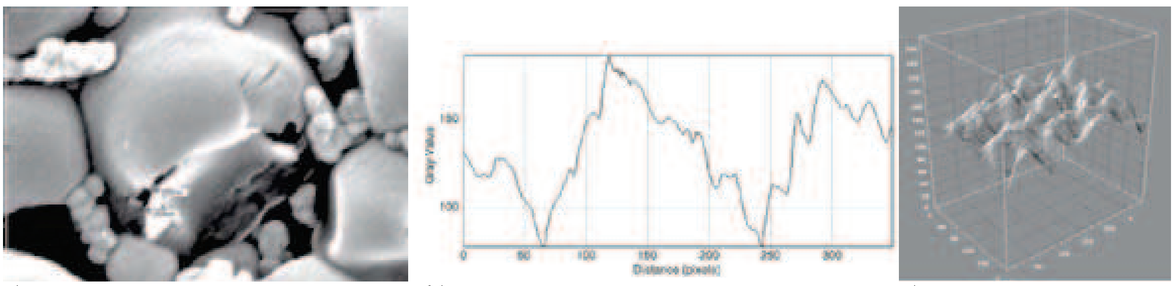
a) b) c)

Figure 25: a) SEM image of microcapsules with no ammonia added (10,000×), b) ImageJ analysis profile, c) Interactive 3D surface plot



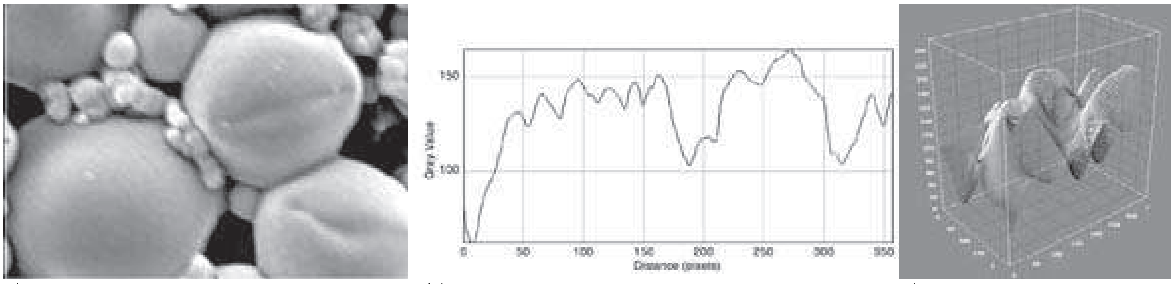
a) b) c)

Figure 26: a) SEM image of microcapsules with 1.35% ammonia added (10,000×), b) ImageJ analysis profile, c) Interactive 3D surface plot



a) b) c)

Figure 27: a) SEM image of microcapsules with no ammonia added (15,000×), b) ImageJ analysis profile, c) Interactive 3D surface plot



a) b) c)

Figure 28: a) SEM image of microcapsules with 1.35% ammonia added (15,000×), b) ImageJ analysis profile, c) Interactive 3D surface plot

effect of ammonia scavenger on the mechanical characteristics and thermal resistance of aminoaldehyde-resin microcapsules, produced by the in situ polymerisation microencapsulation (cf. Figure 29). In addition to reducing residual formaldehyde content, ammonia positively contributed to the microcapsule wall durability and reduced the PCM mass loss from microcapsules. This was an advantage for the microencapsulated PCMs, which have to remain permanently enclosed in the microcapsule and functional over numerous phase transition cycles during the whole product life.

4 Conclusions

Microencapsulation is a knowledge intensive technology, characterised by rapid growth of new publications. A bibliometric analysis reveals that new patents, describing industrial innovations and applications of microcapsules, exceed the number of scientific articles, reporting on new basic research and testing of microcapsules. Microencapsulation is therefore a fast developing and competitive research and industrial domain.

The technique of microencapsulation depends on the physical and chemical properties of the material to be encapsulated, and on the desired characteristics of microcapsules and their functions in the final products. The encapsulated materials are protected, structured and immobilised on a micro-level to be released at precise targeted conditions. The microcapsule morphological properties depend on several process parameters of the microencapsulation process, and are of key importance for the microcapsule

Analiza vzorcev ImageJ je pokazala, da so bile mikrokapsule z 1,35 % dodanega amoniaka bolj enotne, okrogle, z manj poškodbami in nepravilnostmi. Vzorci brez dodanega amoniaka so bili bolj raznoliki, z večjimi razlikami med sferičnimi/celimi in poškodovanimi kapsulami. Opazna je bila večja količina poškodovanih odprtih kapsul. Za določanje morfologije mikrokapsul so se kot uporabne izkazale vse predstavljene analize; pokazale so, da uporaba amoniaka pri izdelavi omogoča pridobivanje boljših, močnejših mikrokapsul.

Za preverjanje opažanj morfoloških sprememb sten PCM mikrokapsul na posnetkih SEM so bile dodatno opravljene gravimetrične analize z izgubo mase pri povišani temperaturi 135 ˚C. Meritve izgube mase PCM iz jedra mikrokapsule so potrdile pozitiven učinek amoniaka na mehanske lastnosti in na toplotno odpornost mikrokapsul z aminoaldehidno polimerno steno (slika 29). Poleg zmanjševanja koncentracije ostankov formaldehida je amoniak pripomogel k boljši obstojnosti sten mikrokapsul ter k manjši izgubi mase PCM iz jedra mikrokapsul. To je bila prednost za

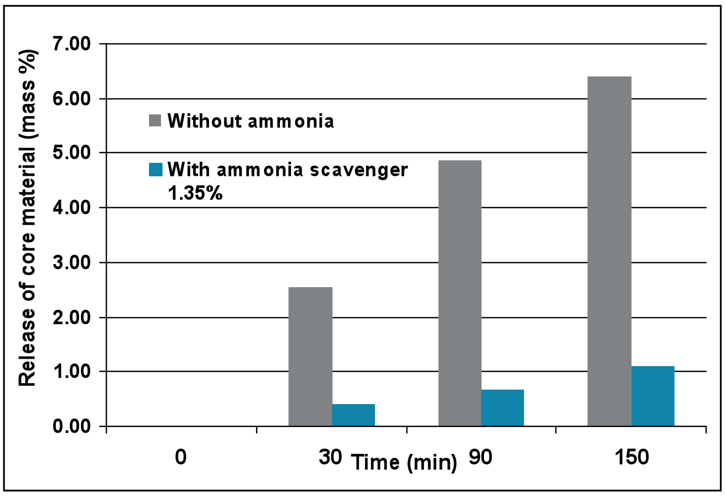


Figure 29: Gravimetric PCM mass loss measurements of microcapsule samples with 0.00 and 1.35% ammonia scavenger in microcapsule suspension after in situ polymerisation process at elevated temperature in ventilated oven (135 °C)

functionality in the final products.
Mechanical tests and chemical analytical methods can precisely determine some characteristics of microcapsules, e.g. mechanical resistance of the material or quantity of residual monomers after the completion of synthesis. However, they cannot directly determine the micro-effects on the microcapsule wall morphology, e.g. deformations and cracking.
In our research, microcapsules of fragrances, antimicrobial agents and phase change materials were produced by the in situ polymerisation of melamine-formaldehyde prepolymers for the applications in textiles. Scanning electron microscopy (SEM) was applied as an effective and environment-friendly morphological analysis tool for a detailed micro-level determination of microcapsules, their morphology, mechanical resistance and distribution on non-woven and woven textiles.
The characterisation of microcapsules with SEM was a successful research tool for:
- *the determination of appearance, morphology, microcapsule size and wall thickness of microcapsules,*
- *the visualisation of microcapsule distribution on non-woven and woven textiles in final R&D products,*
- *the visualisation of mechanical resistance of microcapsule walls on a micro-level, including the deformations and opening of reservoir-type microcapsules, and*
- *the detection of morphological changes of microcapsules (elasticity, deformations and cracking of microcapsule walls) induced by the scavenger during the removal of residual formaldehyde from suspensions at the completion stage of the in situ polymerisation.*

mikrokapsulirane PCM, ki morajo ostati v mikrokapsulah trajno zaprti in ohranjati svojo funkcionalnost v številnih ciklih prehodov agregatnega stanja za celotno življenjsko obdobje izdelka.

4 Sklep

Mikrokapsuliranje je po znanju in tehnologiji zelo hitro rastoče in konkurenčno razskovalno in industrijsko področje z naraščajočim številom novih publikacij. Iz bibliometrične analize je razvidno, da število novih patentov, ki opisujejo industrijske inovacije in aplikacije mikrokapsul, presega število znanstvenih člankov, poroča o novih temeljnih raziskavah in analizah mikrokapsul.

Tehnika mikrokapsuliranja je odvisna od fizikalnih in kemijskih lastnosti materiala, ki ga želimo kapsulirati, ter zaželenih lastnosti mikrokapsul in njihove funkcije pri končnih izdelkih. Mikrokapsulirani materiali so zaščiteni, strukturirani in imobilizirani na mikroravni, da se sprostijo le ob določenih pogojih. Morfološke lastnosti mikrokapsul so odvisne od več parametrov v procesu mikrokapsuliranja ter so ključnega pomena za funkcionalnost končnih izdelkov.

Mehanski testi in kemijske analizne metode lahko podrobno opredelijo nekatere značilnosti mikrokapsul, npr. mehansko odpornost materiala ali koncentracijo ostankov monomerov po opravljeni sintezi, vendar pa z njimi ne moremo neposredno spremljati učinkov na morfologijo sten mikrokapsul, kot so deformacije in razpoke.

V naši raziskavi smo mikrokapsulirali dišave, protimikrobna sredstva in PCM z *in situ* polimerizacijo melamin-formaldehidnih predkondenzatov za aplikacije na področju tekstilstva. Vrstična elektronska mikroskopija (SEM) se je izkazala kot učinkovita in okolju prijazna metoda za podrobno morfološko analizo mikrokapsul, spremljanje njihovih mehanskih lastnosti na mikroravni ter za vizualizacijo mehanske odpornosti in porazdelitve mikrokapsul na tkanih in netkanih tekstilijah.

Karakterizacija mikrokapsul s SEM se je izkazala kot nepogrešljivo raziskovalno orodje za:
- določitev videza, morfologije, velikosti mikrokapsul in debeline sten,
- vizualizacijo porazdelitve mikrokapsul na končnih tkanih in netkanih tekstilijah v končnih izdelkih,
- vizualizacijo mehanske odpornosti sten mikrokapsul na mikroravni, vključno z mehanskimi deformacijami ter odpiranjem rezervoarnega tipa mikrokapsul,
- odkrivanje morfoloških sprememb mikrokapsul (elastičnost, deformacije in pokanje sten mikrokapsul), ki jih je povzročilo dodajanje amoniaka kot lovilca ostankov formaldehida v suspenziji ob koncu *in situ* polimerizacijskega postopka mikrokapsuliranja.

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