

MICROENCAPSULATION IN THE TEXTILE INDUSTRY

The application of microencapsulation techniques offers the possibility of producing novel products with many advantages compared to traditional textile products. The microcapsules can introduce important new qualities to garments and fabrics, such as enhanced stability and the controlled release of active compound(s). Although microencapsulation has found application in other business sectors during the last few decades (food, cosmetics, pharmaceuticals), a significant number of microcapsule-based commercial products appeared in the textile industry during the 1990s, while many potential new products are still in the research and development stage. The most attractive examples are fabrics with durable fragrances, T-shirts with UV-ray absorbing microcapsules, T-shirts with thermo-changeable dyes, military uniforms with microencapsulated insecticide, thermo-regulation vehicle seats, ski suits, and gloves. In spite of important success in developing new products, there is a lot of space for further research, especially in order to improve the mechanical strength of the obtained microcapsules and the kinetics and the mechanism of the release of active compound(s). Therefore, numerous research has focused on the development of new methods of applying of microcapsules on textile, new immobilization techniques and materials, are underway.

Key words: Microcapsule, Textile, Medicine.

Microencapsulation is a process or technique by which microscopic amounts of matter can be entrapped in thin coatings of polymer, thus forming microcapsules. During the last few decades, microcapsules have found applications in the production of a wide range of commercial products, especially cosmetics and pharmaceuticals, because they provide a means of packaging, separating, and storing materials on a microscopic scale for later release under controlled conditions [1]. Microencapsulation offers great opportunities for the improvement of products of textile the industry by the application of additional compounds, such as fragrances, dyes, insect repellents, antimicrobials, or phase changing materials [2]. Therefore, during 1990s there was propulsive research of techniques for obtaining products that can fulfill even the most demanding customer wishes, which resulted in several commercial products and many more in the research and development stage. Consequently, nowadays products, which were just a few decades ago considered to be "science fiction", are available in almost every market. The most illustrative examples are fabrics with durable fragrances, T-shirts with UV-ray absorbing microcapsules, T-shirts with thermo-changeable dyes, military uniforms with microencapsulated insecticide, thermo-regulation vehicle seats, ski suits, and gloves [2–10].

PROCESSING METHOD FOR FABRICS

The main challenge in the process of developing microcapsules with application in the textile industry was

to produce a capsule with adequate mechanical strength to endure the process of application to the textile. Additionally, the obtained microcapsules had to provide the desired mechanism and rate of release of encapsulated compounds, stability and non-toxicity. As wall materials which may satisfy the defined objectives, high polymer materials formed from reactive materials such as monomers or low molecular prepolymers are especially preferred, and examples of such high polymer materials include polyamide resins, polyester resins, polyurea resins, polyurethane resins, urea resins, guanamine resins, melamine resins and complex materials thereof. Such microcapsules were successfully prepared by the solvent evaporation method, interfacial polymerization or fluid bed microencapsulation [2].

Microcapsules can be applied to textiles by padding, coating, spraying or immersion without altering their feel or color. For all these methods, a binder is required. It may be acrylic, polyurethane, silicone, starch, etc. Its role is to fix the capsules onto the fabric and to hold them in place during washing and wear [4,11]. Microcapsules may contain: a perfume, a cosmetic product (moisturizer, freshener, toner), bactericides, a combination of ingredients (for example perfume+bactericide), thermochromes (pigments colour of which changes according to temperature), flame-retardants etc. The textile support may be cotton, silk, nylon, polyester, natural leather, artificial leather, woven, knits, sweaters, yarn and fibers, etc. Also, it can be applied to all types of clothes (suits, casuals, underwear, shirts, blouses, etc.), other clothing (socks, stockings, handkerchieves, gloves, etc.), and its processing method is simple. In the following text the very illustrative example of Aromacap((produced by Kwang Duk Inc.) microcapsule application to textile is given [12].

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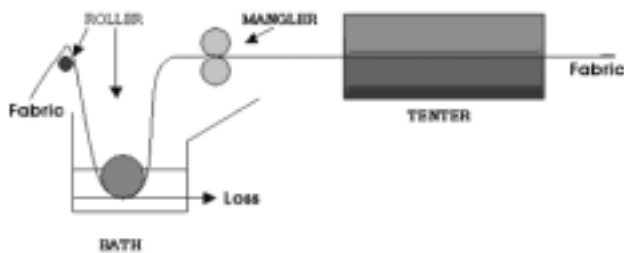


Figure 1. Microcapsule application to textile

The basic process is that the microcapsules are compounded at a certain ratio and padded on the fabric. The microcapsules are attached to the fabric with binder. By evaporating water during the drying process in a tenter, it allows only the required ingredients to combine with the fabric. The structure of the tenter is described in Figure 1.

The roller is equipped so that the fabric can be dipped into the compounded solution. To make solutions for treatment, the microcapsules and binder are added into normal textile chemicals such as softener and anti-static electricity agent, etc. A common mixture contains approximately 2% of microcapsules and 2% of binder. However, the compatibility of the chemicals and microcapsules should be checked in advance (especially the ionic properties).

The mangler plays a role in squeezing the dipped chemicals out of the bath at a certain ratio by the pick up rate when the fabric is passed between two rollers. The heat dryer dries the fabric with heat for evaporating water, and maintaining its width. The characteristic appearance of a textile with microcapsules is illustrated in Figure 2.

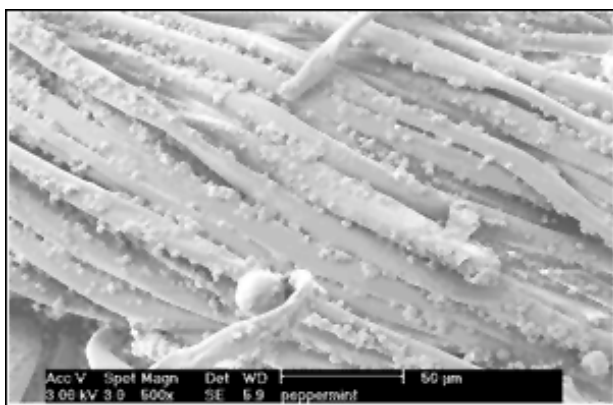


Figure 2. Electron micrograph of fabric after aroma capsules were padded on

PRODUCTS BASED ON MICROENCAPSULATION TECHNOLOGY

Textiles with improved features

Microencapsulation adds new qualities to products of the textile industry because, in contrast to coatings or

laminates, which are applied to the surface of the fabric, encapsulation works inside the fabric, filling the spaces between the fibers with an ultra-thin film of polymer creating a permanent barrier that is breathable, yet impermeable to both water and wind. Encapsulation imparts far greater water repellency, abrasion and stain resistance, and other properties. Nextec Applications Inc.'s is one of the companies focused on using microcapsules for textile products with improved features. The company's line of fabrics, EPIC (Encapsulated Protection Inside Clothing) consists of cotton, stretch nylon and polyester fabrics for use in protective performance outerwear and activewear, as well as in casual sportswear and fashion apparel. The fabric is quick-drying, and allows comfortable, lightweight protection from wind, rain and snow in all but the most extreme heat or cold. The Nextec encapsulation process also has applications for protective medical and industrial uses. Polyester fabrics treated with the Nextec[®] Bio-Barrier System are particularly suitable for high-risk surgical environments that require fluidproof and fluid-repellent protection [13].

Textiles with temperature control system

The new technology called Change Phase (CPMs), already used in the aerospace sector, is nowadays also applied in the textile-clothing area. The principal characteristic of these materials is the capacity to change their aggregation state within a limited temperature (from solid to liquid and vice versa), absorbing or expelling heat. About 500 materials (CPMs) are known, but the most suitable for textile clothing are paraffins enclosed in microcapsules with a diameter of a few microns. Such capsules are then included inside the fibers of traditional textile products, re-covering with thin film or coating through polymer charged with microcapsules. The number of carbon atoms contained in paraffins is directly related to the melting point of the paraffins and, therefore, determines the temperature range in which the product will be active [5,6].

NASA developed the ComforTemp technology that involves the use of microencapsulated phase change materials (Micro PCMs) to provide thermal management properties to a wide variety of materials, including shoes, mountain-climbing boots, undergarments, functional military uniforms, underwear, jackets, sports shoes, ski suits, gloves, car seats, foams, gels, among others. The performance of such new textile materials is the connection of active thermoregulation phenomena that integrate themselves with the passive thermal insulation of traditional fabrics. For example, a ski suit that is finished with heat-storing microcapsules absorbs and stores excessive heat from skiing, thereby preventing the body temperature from rising, and releases the stored heat from the microcapsules to keep the body temperature from falling when riding on the chair lift. These heat-storing microcapsules protect the

body from cold and hot atmospheres by minimizing the range of temperature change that the body can feel [14].

Illustrative examples of fabrics with Change Phase Technology are ComforTemp products with Thermasorb[®] microcapsules (produced by J&C Microchem. Inc.), which have a thin, impermeable plastic shell wall and contain a form of paraffin that is 95-percent pure. In various forms, the paraffin is able to maintain particular temperatures. The materials are continuously "recharged" as the level of activity or surrounding conditions change. The temperatures can be set precisely to suit the intended application.

Textiles with sunscreens and/or antioxidants

Exposure to ultraviolet radiation (UVR) is a well-documented health hazard. When the sun shines on skin, short (290–320 nm) UVB (burning) rays are absorbed by the epidermis. These generate oxygen free radicals, which can destroy and mutate cells and even cause skin cancer. The longer (320–420 nm) UVA (aging) rays go deep into the skin's dermis, and even through the skin. These rays go thirty to forty times deeper than UVB rays, and also generate oxygen-free radicals. UV rays can pass through the clothes, such as white cotton T-shirts, which have a sun protective factor (SPF) between 5 and 9. It is not safe enough for children, soldiers, athletes and people that work outside. Therefore, efforts have been made to develop protective clothes with sunscreens in microcapsules.

The capability of microcapsules to increase the SPF in products without encountering problems of sunscreen solubility or skin sensitivity was thoroughly investigated. An organic sunscreen (14% octyl methoxy-cinnamate [OMC] and 6% oxybenzone) was encapsulated in a benign matrix to form particulates. The encapsulated sunscreens were stable and demonstrated that there was a strong correlation between particle size and UV attenuation. In general smaller particles had greater UV opacity. It was found that there was an increase in the SPF when sunscreens were encapsulated. In addition, as the sunscreen is confined to the capsule, the problem of solubility that is common with high-SPF conventional formulations is averted. Further, decrease in skin irritation as a result of the separation of sunscreen and skin emerged as another advantage of the encapsulated form. In conclusion, microspheres facilitate the formulation of sunscreens and offer the advantages of overcoming solubility and skin irritancy problems.

An innovation from Particle Sciences, Inc., Sun Caps[®] provides a way to incorporate traditional organic sunscreens into virtually any formulation because they substantially reduce most of the formulating difficulties normally associated with organic sunscreens. Each Sun Cap[®] consists of an organic sunscreen, or combination of organic sunscreens, trapped within a matrix. The average particle size is approximately 250 nm. The

organic sunscreen molecules are evenly distributed throughout the particle. Besides sunscreens encapsulated in microcapsules, it is possible to combine sunscreens with vitamin E.

The microcapsule, Vitatek[®] for example, produced by J&C Microchem. Inc. is the most advanced, highly functional product among the vitamins that have a prominent effect on skin health. Vitamin E is microencapsulated and applied to fabrics that directly contact the skin, such as underwear, T-shirts, shirts, blouses, stockings, socks, gloves, bedding, etc. Vitatek[™] can be applied to all types of fabrics since the vitamin is coated to prevent loss of its original function when combined with other materials or by heat due to the fact it is heat-resistant until 220°C. This microcapsule is of the pressure-sensitive type, i.e. the capsules break when they sense a certain pressure. Thus the microcapsules are broken upon friction with the skin and vitamin E is absorbed.

Textiles with polychromic or thermochromic microcapsules

Undoubtedly the most attractive microencapsulated products are those with features of colour change. A very important class of colour changing substances are photochromics. Photochromic inks change from clear when indoors to colored when taken outdoors. They exhibit color in response to exposure to UV light from sunlight, black lights, or similar sources. UV light changes the chemical structure of the photochromic material and makes it absorb colour like a dye. It then reverts to a clear state when the UV source is removed. These inks have found application in colour changing T-shirts.

This product with thermochromic microcapsules changes its colour or becomes colourless or its background colour as the temperature rises, and changes back to its original color as the temperature falls. It can be applied to a variety of products such as printings (temperature marks for cold or hot drinks, product labels, brochures, containers or cups, etc.) fabric dyes or prints, plastics, paints, etc., and it is a highly functional product that plays various and useful roles with its effects of advertising, danger warning, temperature indication, battery check, and so on. Microcapsules which contain thermochromic active substances can be applied to bandages in order to indicate an undesirable increase of temperature in the wound area [15]. The most widely used system for microencapsulation of thermochromic and photochromic inks involves urea or melamine – formaldehyde systems [16].

Textiles with aroma microcapsules

The products are manufactured by micro-encapsulating aroma to control the released amount of aroma and to make the aroma last longer. It can be

applied to almost all industrial products, such as fabrics, papers, plastics, paints, etc., thereby creating scented clothing (clothes, socks, ties), scented stamps, cellular phones, paints, greeting cards, and so on. The microcapsules may comprise natural and synthetic fragrances, perfumes, scents and essences and any other simple substances and mixtures of liquid or powdery compounds insofar as they can rupture by an adequate abrasion to emit fragrance. Fragrances of animal origin, such as musk, civet, castoreum, ambergris or the like, and fragrances of vegetable origin, such as lemon oil, rose oil, citronella oil, sandalwood oil, peppermint oil, cinnamon oil or the like can be incorporated as the natural fragrances. Alternatively, mixed fragrances of, for example, α -pinene, limonene, geraniol, linalool, lavandulol, nerolidol or the like can be used as synthetic fragrances. The fragrant substances are contained in an amount of, preferably 50–95%, by weight, based on the total weight of the microcapsule. A lot of attention has been focused on the improvement of the stability of the obtained microcapsules, especially those for T-shirts. Patents have been reported for products that can endure even up to 25 washing cycles [2,3,15].

From the standpoint of the sustained releasability of fragrant substances and the physical strength of microcapsules, envelope or external wall materials are preferred to be organic polymers, for example, polyurethanes, urea-formaldehyde resins, melamine-formaldehyde resins, cyclodextrin or the like. They are not specifically limited, however, urea-formaldehyde resins and melamine-formaldehyde resins, particularly, low in formaldehyde content, are the most preferred [3,17].

The size of the microcapsules is usually 1–50 μm , preferably 5–20 μm , in average diameter. Particularly, in the case of the wall material being an urea-formaldehyde resin, the particle diameter is 2–50 μm , preferably 5–20 μm , and the wall thickness is 0.1–20 μm , preferably 0.5–4 μm , while in the case of the wall material being a melamine-formaldehyde resin the particle diameter is 5–50 μm , preferably 5–20 μm , and the wall thickness is 0.2–30 μm , preferably about 0.5–6 μm [3,18].

The best binder for the application of these microcapsules to textiles is silicone resin-based binder, especially silicone aqueous emulsion type binders that are dispersible in water and easy to dilute with water, for example, comprising an organopolysiloxane as the main component, emulsified with an emulsifier. More preferable organopolysiloxane emulsions are low temperature reactive type organopolysiloxane prepolymer emulsions. Alternatively, a low temperature reactive blocked isocyanate prepolymer emulsion can be used as a binder in combination with a metallic salt of a fatty acid.

Medicated bandages

The application of microcapsules with antibiotics and other healing substances in bandages provides the

prolonged release of these compounds and infrequent changing of bandages. Medicated bandages consist of a cotton bandage impregnated with a medicament formulated in a moist paste [19]. They are used in the treatment of dermatological conditions, such as eczema and inflammation associated with leg ulcers. Due to this new technology bandages may be left in position for up to 2 weeks. Most are zinc paste bandages containing zinc oxide. Additional ingredients include calamine, coal tar (a fungicide), clioquinol and ichthammol (antibacterials), and parahydroxybenzoates (parabens). A cotton bandage can be impregnated with essential oil formulated in microcapsules.

The microencapsulating of essential oils permits the reduction of loss of the active principles and leads to high-load microparticles, which are able to protect them from environmental agents (particularly light and oxygen) and can offer the possibility of controlled essential oil release. Researchers at the University of Rochester in Rochester, New York, USA, are developing a bandage that changes colour depending on the type of bacteria present in the wound. The bandage will instantly diagnose whether a wound requires special care or what kind of antibiotics may work best in treating it.

Fire retardants

Numerous textile products need to be coated with polyurethane resins in order to improve abrasion resistance and water repellence. Polyurethane coatings on cotton or cotton-polyester blended fabrics are used in many fields such as the transportation industry (car seats) and garments (waterproof jackets, tents), but have bad flame retardancy. Microcapsules offer excellent opportunities for the improvement of the safety of such products. Significant efforts have been made recently in research focused on developing fabrics with microencapsulated fire retardants, particularly di-ammonium hydrogen phosphate [20–22].

CONCLUSION

As can be seen from this brief overview, microcapsules have found numerous applications in various branches of the textile industry, in spite of the fact that related research started in the near past. It resulted with the creation of novel and unique products, which enhance the comfort and relaxation of the user, as well as their safety. Up to now, only the textile industries of USA, Japan and the countries of Western Europe have made progress in this direction, but the propulsive development of microencapsulation techniques all over the world will bring about a future increase of the number of similar products in other countries.

In spite of the existence of such a broad variety of textile products with microcapsules, there is a lot of space for further improvement. The most important properties are the stability of the microcapsules and the kinetics of the release of the active compound(s). The

stability of microcapsules must be increased, especially in clothing products with fragrances, polychromic or thermochromic substances. On the other hand, demands regarding the release of active compound(s) are different for various products. For several applications the continuous slow release of active compound is needed (for example, garments with fragrances or medical bandages with antibiotics), while in a broad range of products (fabrics with PCMs, clothes with sunscreens) the release must be totally prevented or prevented upon the action of significant mechanical force (scratch-and-sniff T-shirts). All of the mentioned inadequacies of existing microcapsules can be improved by developing new polymeric materials for immobilization and developing new, or improving already existing microencapsulation techniques. In addition, alternative, less invasive, ways of applying of microcapsules on textiles should be found.

REFERENCES

- [1] J.D. Dziezak, Microencapsulation and Encapsulated Ingredients, *Food Technol.* **42** (1988), 136–151.
- [2] G. Nelson, Application of microencapsulation in textiles, *Int. J. Pharm.* **242** (2002) 55–62.
- [3] A. Ono, T. Fuse, O. Miyamoto, S. Makino, Y. Yamato, H. Kametani, S. Tokura, H. Tanaka, T. Ito, H. Nakao, S. Tokuoka, T. Takeda, Fibrous structures having a durable fragrance and a process for preparing the same, US Patent 4,917,920 (1990).
- [4] Y. Yamato, T. Yoshida, M. Kikuchi, M. Okamoto, K. Miyoshi, S. Fukuda, T. Fuse, T. Yamauchi, Y. Ogawa, S. Mutagami, S. Shiomura, Y. Mizukami, Microcapsule, treating liquids containing the same, and textile structure having microcapsules adhering thereto, US Patent 5,232,769, (1993).
- [5] F. Fourrey, Method and system of regulating heat in a vehicle seat, US Patent 6,291,803 (2001).
- [6] J. Zuckerman, R. Pushaw, B. Perry, D. Wyner, Fabric coating composition containing energy absorbing phase change material, US Patent 6,207,738 (2001).
- [7] R. Samson, J. McKinney, J. Russell, Fabrics with insect repellent and a barrier, US Patent 5,252,387 (1993).
- [8] R. Samson, J. McKinney, J. Russell, Insect repellent tent fabric, US Patent 5,198,287 (1993).
- [9] A.K. Aggarwal, A. Dayal, N. Kumar, Microencapsulation processes and applications in textile processing, *Colourage* **45** (1998) 12–22.
- [10] G. Erkan, M. Sarişik, Microencapsulation in textiles, *Colourage Annual* (2004), 61–64.
- [11] S. Nelsen, E. Wotier, D. Alwani, Y. Ozari, Core-shell polymers, 4,264,678 (1981).
- [12] www.microcapsule.com (Updated: 2002)
- [13] www.nextec.com (Updated: 2003)
- [14] www.comfortemp.com (Updated: 2003)
- [15] www.colorchange.com.tw (Updated: 2004)
- [16] D. Aitken, S. M. Burkinshaw, J. Griffiths, A. D. Towns, Textile applications of thermochromic systems, *Rev. Prog. Color* **26** (1996) 1–8.
- [17] K. Hong, S. Park, Melamine resin microcapsules containing fragrant oil: synthesis and characterization, *Mater. Chem. Phys.* **58** (1999) 128–131.
- [18] R. Williamson, N. Derby, C. Nickell, Anti-microbial shoe linings, sock liners and socks and process for manufacture of same, US Patent 6,139,669 (2000).
- [19] S. Chandrasekaran, Therapeutic system for administering drugs to the skin, US Patent 4,286,592 (1981).
- [20] N.S. Zubkova, A highly effective domestic fire retardant for fireproofing fibrous textile materials, *Fibre. Chem.* **29** (1997) 126–129.
- [21] S. Giraud, S. Bourbigot, M. Rochery, I. Vroman, L. Tighzert, R. Delobel, Microencapsulation of phosphate: application to flame retarded coated cotton, *Polym. Degrad. Stabil.* **77** (2002) 285–297.
- [22] S. Giraud, S. Bourbigot, M. Rochery, I. Vroman, L. Tighzert, R. Delobel, F. Poutch, Flame retarded polyurea with microencapsulated ammonium phosphate for textile coating, *Polym. Degrad. Stabil.* **88** (2005) 106–113.

IZVOD

MIKROINKAPSULACIJE U TEKSTILNOJ INDUSTRIJI

(Naučni rad)

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Primenom tehnika mikrokapsulacije otvara se mogućnost proizvodnje novih proizvoda sa mnoštvom prednosti u odnosu na tradicionalne proizvode tekstilne industrije. Primenom aktivnih supstanci u obliku mikrokapsula na odevne predmete dobijaju se potpuno nove osobine, poput kontrolisanog otpuštanja aktivne supstance i njene povećane stabilnosti. Iako je mikrokapsulacija u toku prethodnih nekoliko decenija našla primenu u drugim privrednim granama (prehrambena, kozmetička i farmaceutska industrija) komercijalni tekstilni proizvodi koji sadrže mikrokapsule počeli su da se pojavljuju tek tokom 90-tih godina prošlog veka, a mnoštvo novih potencijalnih proizvoda je u fazi istraživanja i razvoja. Najatraktivniji primeri su: majice sa inkapsuliranim mirisnim supstancama, majice koje menjaju boju pri promeni temperature, majice koje apsorbiraju UV zračenje, vojne uniforme sa inkapsuliranim insekticidima, automobilska sedišta i skijaška odela sa regulacijom temperature. Iako je razvijeno mnogo novih proizvoda, postoji potreba za daljim istraživanjem naročito u cilju poboljšanja mehaničkih osobina mikrokapsula i boljeg kontrolisanja kinetike otpuštanja aktivne susptance.

Ključne reči: Mikrokapsule, Tekstil, Medicina.