Microencapsulation technology and its applications in building construction materials

Tehnologija mikrokapsuliranja in njena uporaba v gradbenih materialih

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Abstract: The article is a review of microencapsulation types, technologies, purposes of microencapsulation, release mechanisms, and application fields, with special emphasis on microencapsulated additives in building construction materials. The following improvements have been described in patents as a result of microencapsulated additives in the construction materials: increased fireproofing; improved freeze- and freeze-thaw resistance; reduced expansion and degradation of concrete and mortar; better hydration of concrete and mortar mixes in the compression-molding production of building elements; reduction of thermal cracking due to the heat release by cement hydration; decrease of water absorption of hydraulic cement sheets; insulation or absorption of noise; protection of building materials against mildew, bacteria, insects, rodents and environmental corrosion; fragranced / deodorising effect; and reversible thermochromic colour changes of cement-based materials for darker building exteriors in winter and lighter colours in summer. The fastest growing segment is that of insulating materials based on microencapsulated phase change materials (PCM) for active accumulation and release of heat. Microcapsules with a good mechanical resistance are essential to enable reversible liquid-solid-liquid phase transitions, and to protect the PCM during the whole product life.

Izvleček: Pregledni članek podaja tipe, tehnologije in namene mikrokapsuliranja, mehanizme sproščanja ter področja uporabe s podrobnejšim pregledom uporabe mikrokapsuliranih dodatkov v gradbenih materialih. V patentih so opisane naslednje izboljšave, dosežene s pomočjo mikrokapsuliranih aktivnih komponent: izboljšana protipožarna zaščita in negorljivost materialov; zmanjšano raztezanje in propadanje betona; preprečevanje razpok zaradi sproščanja toplote med hidracijo cementa; omogočanje hidracije cementnih izdelkov med proizvodnjo v stiskalnicah; zmanjšana vodna vpojnost cementnih plošč; zvočna izolacija in absorpcija zvoka; varovanje gradbenih materialov pred pojavom plesni, bakterij, insektov, glodalcev; zaščita pred korozijo; odišavnjenje in deodoriranje materialov; reverzibilne toplotne spremembe barv, ki omogočajo temnejšo barvo fasade pozimi in svetlejšo barvo poleti. Najhitreje razvijajoči se segment uporabe mikrokapsul so izolacijski materiali, ki temeljijo na fazno spremenljivih materialih (PCM) za aktivno akumulacijo in sproščanje toplote pri prehodih agregatnega stanja tekoče-trdno-tekoče. Mikrokapsule z dobro mehansko odpornostjo premoščajo problem reverzibilnih faznih prehodov in omogočajo varno zadrževanje PCM v gradbenem materialu skozi vso življensko dobo izdelka.

Key words: microencapsulation, microcapsules, applications, building, construction, materials

Ključne besede: mikrokapsuliranje, mikrokapsule, uporaba, gradbeništvo, materiali

Microencapsulation technology

Microencapsulation is a technology of coating small particles of finely ground solids, drops of liquids, or gaseous components, with protective membranes – microcapsule walls (Deasy, 1984; Arshady & Boh, 2003). 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 hydrophobic solutions of leuco dyes (Fanger, 1974). Since then, microencapsulation has been constantly improved, modified and adapted for a variety of purposes and uses. As a consequence, it has become an example of a knowledge-intensive and dynamic technology (Boh & Kardoš, 2003), characterised by a rapid growth of patent applications, reflecting industrial research and development, as well as by an increasing number of new scientific articles, deriving from the basic research (Figure 1). 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 (Boh et al., 2003; Boh, 2007; Poncelet & Boh, 2008).

Several physical and chemical methods have been developed for the production of microcapsules (Arshady, 1999; Vandamme et al., 2007). The most often used microencapsulation methods are (Boh, 1996a,b):

- **mechanical methods** (e.g. spray drying, pan coating, and 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 (Figure 2), and

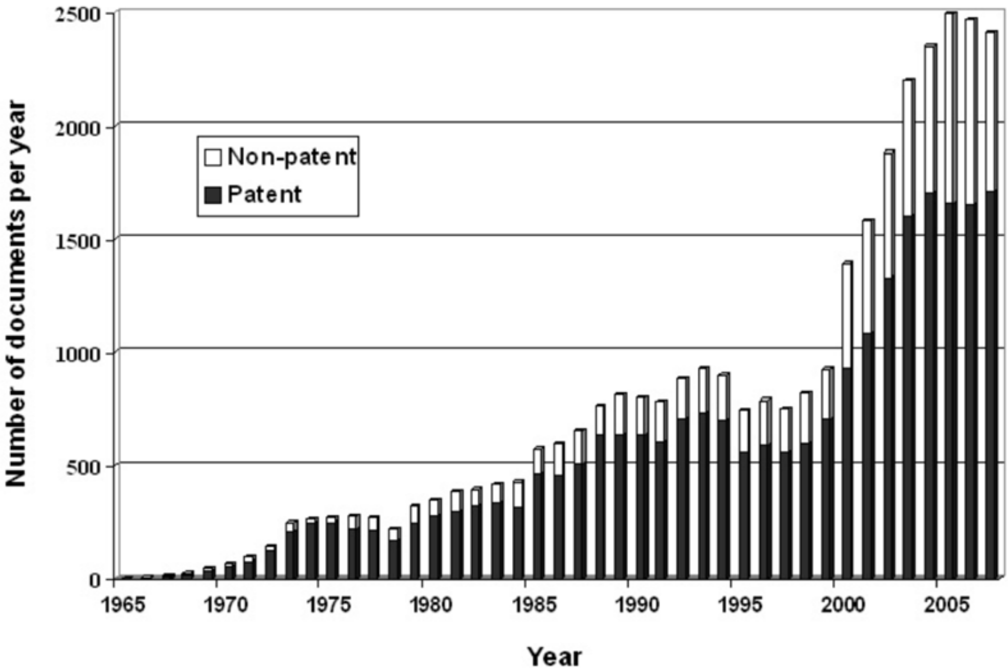


Figure 1. Growth of new patent documents and scientific articles on microencapsulation (CA Plus database)
Slika 1. Rast števila patentnih dokumentov in znanstvenih člankov na področju mikrokapsuliranja

- **polymerisation methods**, where monomers polymerise around droplets of an emulsion and form a solid polymeric wall. In **polymerisation *in situ*** monomers or precondensates are added only to the aqueous phase of emulsion (Figure 3), while in **interfacial polymerisation,** one of the monomers is dissolved in the aqueous phase and the other in a lypophylic solvent (Figure 4).

Due to the development and specialisation of microencapsulation technologies and applications, microencapsulation products differ in structure and terminology (Table 1), (Boh, 1996a,b).

Purposes of microencapsulation and release mechanisms

Different purposes of microcapsule-based final products require different characteristics of microcapsules. The size and shape of microcapsules, chemical properties of microcapsule walls, and their degradability, biocompatibility and permeability have to be considered in the selection of raw materials and microencapsulation processes. The purpose of microencapsulation is usually defined by the permeability. Microcapsules with **impermeable walls** are used in products where isolation of active substances is needed, followed by a quick release under defined conditions.

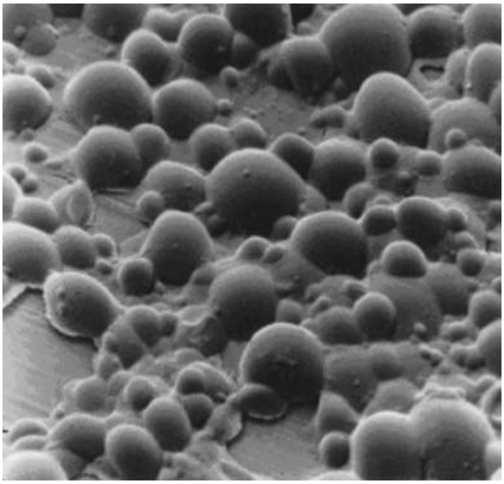


Figure 2. Coating of microcapsules, produced by complex coacervation of gelatin and carboxymethyl cellulose (scanning electron micrograph, 630 x), (Boh, 1986)
Slika 2. Premaz mikrokapsul, izdelanih po postopku kompleksne koacervacije želatine in karboksimetil celuloze (elektronski mikroskop, 630x), (Boh, 1986)

The effects achieved with impermeable microcapsules include: separation of reactive components, protection of sensitive substances against environmental effects, reduced volatility of highly volatile substances, conversion of liquid ingredients into a solid state, taste and odour masking, and toxicity reduction. On the other hand, microcapsules with **permeable walls** enable prolonged release of active components into the environment, such as in the case of prolonged release drugs, perfumes, deodorants, repellents, etc., or immobilisation with locally limited activity of microencapsulated substances. Examples of later include microencapsulated fertilizers and pesticides with locally limited release to reduce leaching into the ground water, or microencapsulated catalysts and enzymes for chemical and biotechnological processes (Boh, 1996a,b).

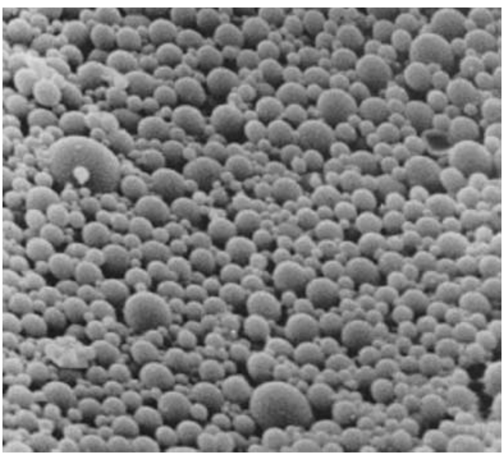


Figure 3. Coating of microcapsules, produced by in situ polymerization of aminoaldehyde precondensates (scanning electron micrograph, 1900x), (Knez, 1988; Kukovič & Knez, 1996)
Slika 3. Premaz mikrokapsul, izdelanih z in situ polimerizacijo aminoaldehidnih predkondenzatov (elektronski mikroskop, 1900x), (Knez, 1988; Kukovič & Knez, 1996)

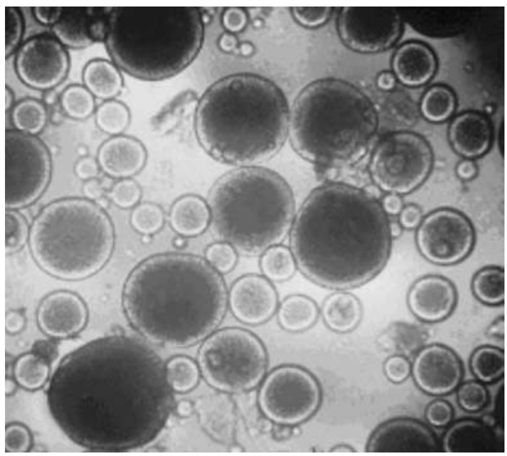
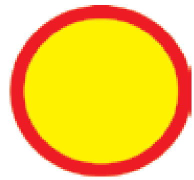
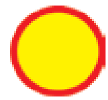


Figure 4. Suspension of microcapsules, produced by interfacial polymerization - crosslinking of proteins in a water-in-oil emulsion (light microscopy, 100x), (Boh, 1991)
Slika 4. Suspenzija mikrokapsul, izdelanih po postopku medpovršinske polimerizacije z zamreževanjem beljakovin v emulziji tipa voda v olju (optični mikroskop, 100x), (Boh, 1991)

Table 1. Terminology of microencapsulation products
Tabela 1. Poimenovanje produktov mikrokapsuliranja

Terminology	Description	Size range	Schematic illustration
Microcapsules (narrow sense of meaning)	Products of coating liquid nuclei with solid walls.	µm	
Nanocapsules	Same structure as microcapsules, but smaller.	nm	
Microspheres or microparticles	The cores and walls are both solid. Often, there is no clear distinction between them: the thick solid wall functions as a porous matrix where active substances are embedded.	µm	
Nanospheres or nanoparticles	Same structure as microspheres, but smaller.	nm	
Liposomes **Niosomes**	Lipid wall, often made of phospholipids and cholesterol. Subtypes: unilamellar (one lipid layer) and multilamellar (several lipid layers). Similar to liposomes but their membranes are made of synthetic amphiphylic molecules (detergents).	µm to nm	 

The **mechanisms of releasing encapsulated materials** are planned in advance and depend on the purpose of microencapsulation. An analysis of several hundred patent documents (Boh, 1996a,b; Poncelet & Boh, 2008) revealed that the first developed and still often used is the mechanism of **external pressure** which breaks the microcapsule wall and releases the liquid from the core. This principle is applied in pressure-sensitive copying papers (pressure of the pen-ball or typewriter head), multi-component adhesives (activation in a press), deodorants and fungicides for shoes (mechanical pressure caused by walking), polishing pastes (rubbing) and aromas and sweeteners in chewing gums (chewing). In some applications, the microcapsule wall breaks because of **inner pressure**, e.g. for blowing agents in the production of light plastic materials and synthetic leather. In instant drinks, microcapsules **dissolve** in water. Dissolution at the selected pH value is useful for microencapsulated catalysts and pharmaceuticals. Drugs, vitamins, minerals, essential amino acids, fatty acids, or even whole diets, can be released into the gastro-intestinal tract by **enzymatic degradation** of digestible microcapsules. The core substance can be released by **abrasion** of the microcapsule wall, e.g. in antistatics and fragrances for textiles (abrasion in washing machines and dryers), or for grinding and cutting additives. In many applications, core materials are released by **heat.** Heat-sensitive recording papers (e.g. telefax paper), temperature indicators for frozen food, heat-sensitive adhesives, textile softeners and fragrances in formulations for dryers, cosmetic components to be released at body temperature and aromas for tea and baking, are based on the effect of melting of the microcapsule wall. Microencapsulated fire retardants or extinguishers, based on release caused by **burning** of microcapsule walls, are used in fire-proof materials. These types of microcapsules are used for wall paper, carpets, curtains, fire-protecting clothes, and added to plastics and coatings for electric devices and wires. Microcapsules in special photographic emulsions, light-sensitive papers and toners for photocopiers are decomposed (or hardened) by **light**. If the wall is **permeable**, it **slowly releases** the content of the core. This mechanism can be applied in controlled drug release products, aromas, fragrances, insecticides and fertilisers. In the case of microencapsulated cells and enzymes in biotechnology, high-molecular weight components can be retained in microcapsules, while low-molecular by-products and substrate residues are **extracted** through **semi-permeable** microcapsule walls. A special example is that of microencapsulated phase change materials for active accumulation and release of heat in textiles, shoes and building insulation materials. To remain functional over numerous phase transition cycles, they have to **remain encapsulated** within the impermeable and mechanically resistant microcapsule wall for the whole product life.

Applications of microcapsules in building construction materials

An analysis of scientific articles and patents shows numerous possibilities of adding microencapsulated active ingredients into construction materials, such as cement, lime, concrete, mortar, artificial marble, sealants, paints and other coatings, and functionalised textiles. A summary of applications is presented in Figure 5.

Fireproofing

Composite fire-resistant and lightweight building boards were patented (Adachi, 2005), containing a flammable substrate and a fireproofing Portland cement, which contained a foaming agent for generating an incombustible gas, a carbide layer precursor, and a microencapsulated carbide formation catalyst. The product was suitable for interior and/or exterior building boards. In another invention (Parthy, 2003) microencapsulated water was used for increasing fire resistance of construction materials. Microencapsulated water was added to gypsum plaster boards, paints, or thermal insulating materials.

Freeze and freeze-thaw resistance

To improve freeze and/or freeze-thaw resistance, microencapsulated sterically or electrostatically repelling monomers were added into hydraulically setting building materials, such as cement, lime, gypsum, anhydrite binders, as well as mortar or concrete mixtures (Schattka et al., 2007). Zhang (2005) patented the manufacture of an efficient and environmentally friendly snow-thawing composition, containing microencapsulated percarbamide as a snow-thawing active component.

Expansion and degradation resistance

To reduce expansion and to prevent degradation of concrete and mortar by alkali-aggregate reaction, a patent by Miyazawa and Akiyama (1988) suggested an addition of microcapsulated mineral oils or surfactants into construction material mixes. In a test, the expansion of the mortar product after 3 months was 0.127 %, vs. 0.41 % without the microcapsules.

Hydration of concrete and mortar mixes

Tomiuchi and Nishihama (1986) patented applications of microencapsulated water in the production of building boards with uniform strength. Typical compositions consisted of cement, mixed with fiber (e.g., asbestos, synthetic fiber) and microcapsules containing water for hardening. Building boards with uniform strength were manufactured on a belt conveyer by compression-molding, resulting in cement hardening. In another invention (Noda Plywood Mfg. Co., Ltd, 1985) high strength building boards were manufactured from a mixture of hydraulic material (gypsum), fibrous material, additives, and gelatine microcapsules containing water glass as a setting accelerator. Setting retardant and excess water were added, the mixture was poured into molds, pressed to remove access water and release the accelerator, and set. Microencapsulated or gelled water was used in cartridges of quick-setting cement (Heinen & Babcock, 1988). A premixed mortar mixture was patented, consisting of cement and microcapsules containing water (Origasa et al., 1988). In a patent by Okamoto et al., (1989) on manufacturing concrete and mortar mixes, water was encapsulated in an acrylate superabsorbent polymer. In the production of concrete or mortar, the water was released from the superabsorbent by molding to promote hydration of the surrounding cement.

Reduction of hydration heat release

Mass concrete suffers from thermal cracking due to heat release by cement hydra-

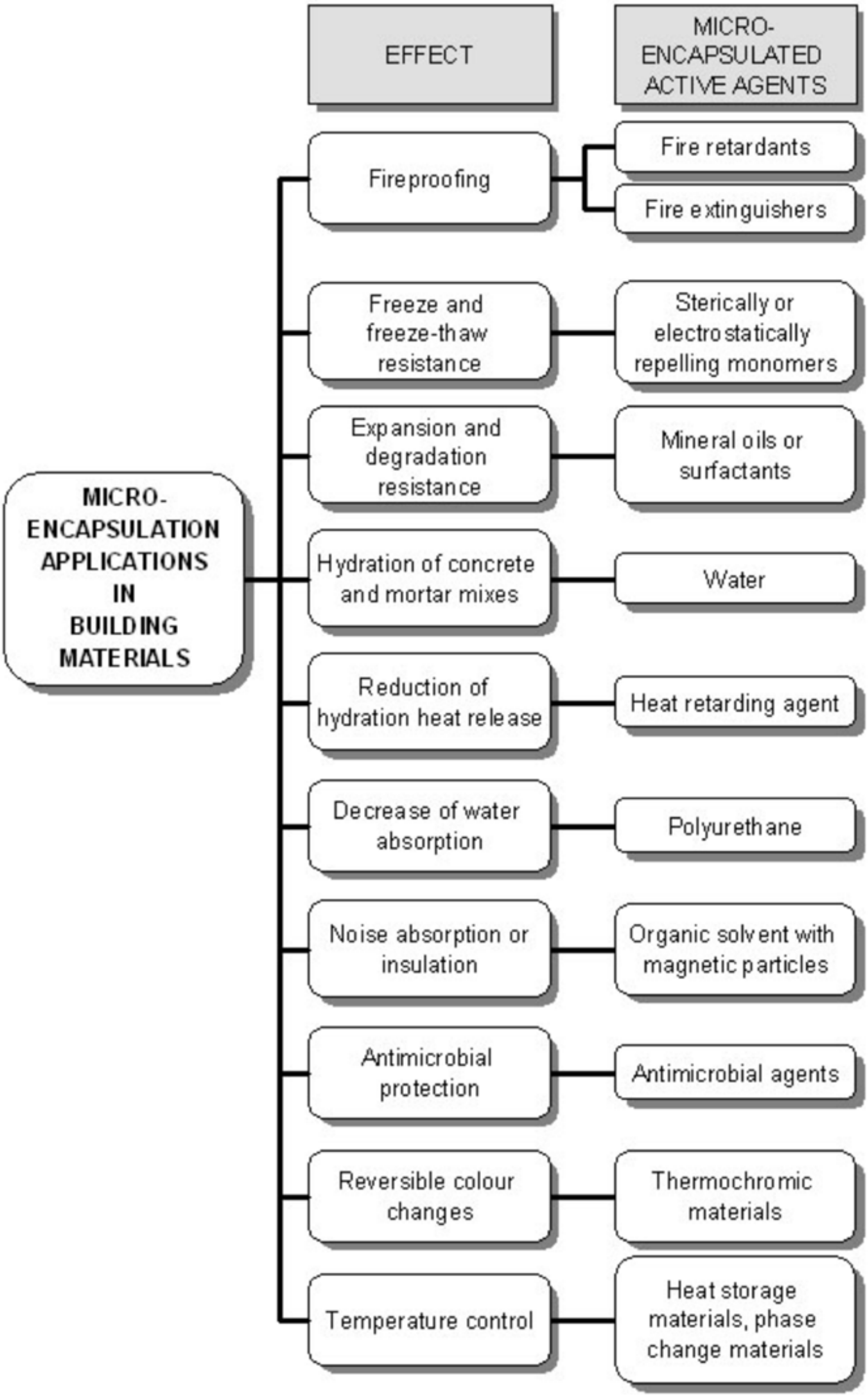


Figure 5. Applications of microcapsules in building construction materials
Slika 5. Uporaba mikrokapsul v gradbeništvu

tion. Using low heat Portland cement or fly ash cement was proposed as a countermeasure against this problem. The problem was also addressed in a study by Takeuchi et al., (2007). Wax microcapsules were developed, in which very fine solid particles of a retarder were included. When wax microcapsules melted at a designed temperature, the retarder was released into the cement matrix and it controlled the rate of heat release by cement hydration. Microcapsules remarkably reduced the hydration heat release rate and the adiabatic temperature rise speed of the cement mortar.

Decrease of water absorption

In the production of hydraulic inorganic sheets, 5-20 % of microcapsules containing polyurethane resin were added to the aqueous slurry of a blast-furnace slag cement and ettringite. The sheets were molded and hardened. Microencapsulated additive decreased the water absorption by 15-20 % (Matsushita Electric Works, Ltd., 1982).

Noise absorption or insulation

Microcapsules containing a magnetic fluid were used to absorb or insulate noise. Examples included noise-absorbing thermally expanding microcapsules, made of a thermoplastic resin, which contained a hydrophobic organic solvent with 5-200 nm magnetic particles, and a hydrophobic liquid foaming agent. The noise-absorbing microcapsules were incorporated into paints, and mixed in or adhesively attached to construction materials (Tanaka et al., 1997).

Antimicrobial protection

Microcapsulated essential oils of a white cedar were used in a mixture with a binder to protect building walls against generation of mildew (Arai, 2001). In a patent by Higashizaka (2002a,b, 2004), sustained release microcapsules containing hinokithiol were applied to protect leveling or base concrete in building construction against insects, bacteria, and corrosion, and to achieve a deodorising effect. A patent by Nishiguchi et al., (1998) described incorporation of microencapsulated fragrances, deodorants, antibacterial agents or insecticides into Calcium silicate shaped products for building interiors and exteriors.

Reversible colour changes

Several patents by Ma (2006a,b,c, 2007) described reversibly thermochromic cement-based materials, prepared by adding reversibly thermochromic microcapsules into a white Portland cement. Microencapsulated special thermochromic agents changed reversibly from blue, red or green colour at a lower temperature to white at a higher temperature. The system enabled a reversible change of colours: buildings were darker in winter, to absorb heat, and white in summer, to reflect the light energy.

Temperature control

Microcapsules containing latent heat storage materials, especially phase change materials, have been used to improve the heat storage capacity of buildings.

Phase Change Materials (PCMs) are a subgroup of heat Storage Materials (HSMs), with a dynamic heat exchange process taking place at the melting point temperature. When a PCM undergoes a phase change transition from solid to liquid, energy is stored in the form of latent heat at a constant temperature. Accumulated latent thermal energy is released when the PCM solidifies again. In general, the higher the PCM's latent heat of phase change is, the more thermal energy a material can store. The transition process is completely reversible.

Typical organic PCMs are higher hydrocarbons (paraffins and their narrow fractions) (He & Setterwall, 2002; Hawlader et al., 2002; Hummel & Stich, 2003), as well as waxes, higher alcohols and higher fatty acids (Feldman et al., 1986, 1989; Suppes et al., 2003). The melting points of straight chain higher hydrocarbon PCMs depend on the length of the carbon atom chains, i.e. on the number of carbon atoms in the molecule. Higher hydrocarbons with 13 to 28 carbon atoms have phase change temperatures ranging from – 5.5 °C to + 61 °C. Compared to other PCMs, they have a high energy storage density, high boiling points and stability up to 250 °C. They are chemically inert, non-corrosive, long-lasting, inexpensive, ecologically harmless and non-toxic. These characteristics have made them the preferred PCMs for many commercial applications.

To overcome practical problems of solid-liquid phase transitions, PCMs have to be microencapsulated and turned into solid formulations for applications in various thermal management applications. To remain functional over numerous phase transition cycles, microencapsulated PCMs have to remain encapsulated within the impermeable microcapsule walls for the whole product life. PCM microcapsules need to be highly resistant to mechanical and thermal stress, which is achieved by improved or new microencapsulation methods. Holman (2001) patented gel-coated microencapsulated PCMs, consisting of a polymeric wall and a continuous metal oxide gel, resulting in an improved mechanical stress and flame resistance. Momoda and Phelps (2002) reported that nanoencapsulated PCMs with reversible high thermal transport properties at elevated temperatures can be used in low viscosity heat transfer fluids at sub-freezing temperatures. Another method of making microcapsules has been developed (Vasishtha, 2003), using microwaves as a source of electromagnetic energy, in combination with core and wall materials of different dielectric constants and dissipation factors.

Several temperature management systems have been developed and patented with microencapsulated PCMs for building applications. Examples include building elements for reduction of temperature oscillations in buildings, containing microencapsulated PCMs sealed within the concrete or plaster matrix structure (Chahroudi, 1981), and building conditioning systems for ceiling and floor surfaces (Pause, 2001). Tanaka and Suzuki (1997) patented microencapsulated paraffin phase change materials as additives to fresh concrete mix, mortar, or cement paste in the production of molded building products.

Inventions by Ishiguro (1998, 2003, 2004a,b, 2005, 2006) were based on the incorporation of microencapsulated heat storage materials into building insulation materials, such as laminated gypsum boards. In a typical example, one or both sides of the gypsum board were laminated with a heat-storage sheet, obtained by dipping the board into a microencapsulated heat storage material. Patents by Matsushita and co-workers (Matsushita et al., 2002a,b; Matsushita & Ishiguro, 2003; Matsushita & Sato, 2003) described hydraulic compositions for production of latent heat-storable building materials. Typical compositions contained cement or gypsum, and microencapsulated latent heat storage materials. Iguchi et al., (2005) patented the application of microencapsulated heat storage materials in road construction materials, suitable especially for bridges, to suppress freezing in the winter time, or the heat island phenomenon in the summer time. Patents by Schmidt and co-workers (Schmidt & Volkmann, 2005; Schmidt & Schmidt, 2006) described a composite element made from a rigid polyurethane foam and two outer layers. At least one outer layer was molded (made of gypsum, lignocellulose, aminoplast resin, phenolic resin, urea-formaldehyde resin, and/or melamine-formaldehyde resin), and contained microencapsulated latent heat storage material. Hu and co-workers (Hu et al., 2007) patented sodium alginate for the microencapsulation of heat storage materials. Microcapsules were incorporated into gypsum.

Conclusions

Microencapsulation is a knowledge-intensive technology with a rapid growth of publications. A bibliometric analysis in the Chemical Abstracts Pus database shows that per each new scientific article on microencapsulation there are at least two patent applications, which illustrates the intensity of industrial research and innovation in the field. Microcapsules have been used in paper and printing industries, adhesives for technical purposes, textiles, pharmaceutical and medical applications, food industry, biotechnology, chemical industries, agrichemicals, photography, and electronics.

Microencapsulation applications are also entering into the field of building construction materials. Analysis of patents identified the following improvements achieved by microencapsulated additives in the construction materials: fireproofing by microencapsulated fire retardants or fire extinguishers; improved freeze- and freeze-thaw resistance; reduced expansion and degradation of concrete and mortar; hydration of concrete and mortar mixes in the compression-molding production of building elements; reduction of thermal cracking due to heat release by cement hydration; decrease of water absorption of hydraulic cement sheets; insulation or absorption of noise; protection of building materials against mildew, bacteria, insects, rodents and environmental corrosion, and achieving a fragranced / deodorising effect.

Special applications are microencapsulated thermochromic agents, which enable reversible colour changes of cement-based materials, e.g. for darker building exteriors in winter, to absorb heat, and for white colour in summer, to reflect the light energy. The fastest growing segment of microencapsulated additives in construction materials are latent heat storage materials for temperature control, especially the paraffinic phase change materials with a high energy storage density. Microcapsules with a good mechanical resistance are essential to enable reversible liquid-solid-liquid phase transitions and to protect the PCM during the whole product life.

Povzetek

Tehnologija mikrokapsuliranja in njena uporaba v gradbenih materialih

Mikrokapsuliranje je tehnologija z velikim deležem znanja in hitrim naraščanjem števila publikacij. Bibliografska analiza v podatkovni bazi Chemical Abstracts Plus kaže več kot dvakrat večje število patentnih prijav v primerjavi z znanstvenimi članki, kar nakazuje intenzivnost industrijskih raziskav in aplikacij mikrokapsuliranja. Mikrokapsule uporabljajo v industriji papirja in tiska, v tekstilstvu, v farmacevtskih in medicinskih izdelkih, v živilski industriji, biotehnologiji, kemiji, za večkomponentna lepila, v proizvodnji fitofarmacevtskih sredstev, v fotografiji in elektrotehniki.

Aplikacije tehnologije mikrokapsuliranja se širijo tudi na področje gradbeništva. Analiza patentnih dokumentov je identificirala naslednje možnosti izboljšav, ki jih prinaša uporaba mikrokapsuliranih dodatkov v gradbenih materialih: negorljivi materiali z vsebnostjo mikrokapsuliranih zaviralcev gorenja; izboljšana odpornost proti zamrzovanju, taljenju in korozivnemu razpadu; zmanjšano raztezanje in krčenje ter posledično pokanje betona in ometov zaradi dejavnikov okolja ali zaradi termičnih sprememb ob hidraciji cementa; vlaženje suhih zmesi betona in malte z mikrokapsulirano vodo pod pritiskom v kalupih; cementni izdelki z manjšo absorptivnostjo vode; izboljšana zvočna izolacija oz. močnejša absorpcija zvoka; zaščita gradbenih materialov pred glivami, bakterijami, insekti, glodalci, korozijo zaradi okoljskih dejavnikov; odišavljenje in deodoriranje materialov.

Posebne aplikacije tehnologije mikrokapsuliranja so termokromni dodatki, ki omogočajo reverzibilne barvne spremembe cementnih izdelkov. Primer so zunanje površine zgradb, ki so pozimi temne, da absorbirajo več toplotne energije, ter bele poleti, da sončno svetlobo čim močneje odbijajo. Najhitreje rastoči segment mikrokapsuliranih aditivov v gradbenih materialih so materiali za latentno akumulacijo toplote. Med njimi so v ospredju parafinski fazno spremenljivi materiali (PCM – Phase Change Materials) z visoko toplotno kapaciteto. Zaradi nenehnih reverzibilnih prehodov agregatnega stanja trdno-tekoče je za praktično uporabo PCM ključnega pomena mikrokapsuliranje v mikrokapsule z dobro mehansko in termično odpornostjo.

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