Microencapsulation of phase change materials by *in situ* polymerisation

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Introduction

Phase Change Materials (**PCMs**) are a sub-group 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.

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.
Typical organic PCMs are higher hydrocarbons (paraffins and their narrow fractions), as well as waxes, higher alcohols and higher fatty acids. 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^{o}C to $+61^{o}$C. Compared to other PCMs, they have a high energy storage density, high boiling points and stability up to 250^{o}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.

In **textile** applications, microcapsules with PCMs have been incorporated into fabrics with enhanced thermal properties, functioning as heat absorbers or as barriers against cold in diving suits, fire wear, special working clothes, military uniforms, sportswear, leather products, gloves and shoes. In **building construction materials**, microencapsulated PCMs have been incorporated into concrete, plaster or synthetic polymers in the production of building elements, conditioning systems for ceiling and floor surfaces, insulation panels, and fresh mixes of concrete, mortar, or cement for moulding. In **medical applications**, patents describe microencapsulated PCMs in medical orthopaedic support materials, composites for transporting temperature-sensitive pharmaceutical materials, body armours for protection against blunt injury trauma, warmable bandages for promoting wound healing, support surfaces for skin cooling and reducing the incidence of bedsores, heating or cooling pads and gloves for reducing pain or swelling, and cooling body wraps for rapidly inducing hypothermia. Other **high-tech applications** of microencapsulated PCMs include environmental microclimate control systems for vegetation and seeds in agriculture; active cooling systems for electronic devices, such as lap-top computers, materials for aircraft brake disks, infrared radiation absorbing materials used for camouflaging objects emitting infrared radiation, and invisible markings systems for mail.

Materials and methods

Laboratory microencapsulation experiments were performed in a 1 L stainless steel reactor (Volrrath), diameter 150 mm, equipped with 5 exchangeable dissolver stirrers of different diameters

(90, 70, 60, 55, 45 mm) with impeller speed 1200 to 6000 rpm, and a cooling/heating system. For process scaling-up, a 10 L stainless-steel pilot reactor was used, with a diameter of 300 mm, double outer walls for heating/cooling operations, equipped with a 0.25 KW electric motor for a dissolver stirrer (diameter 75 mm, 0 - 2800 rpm, continuous adjustment), and a 0.25 KW electric motor for anchor stirrer with teflon scrapers (25 rpm).

Partly methylated trimethylolmelamine (TMM) (Melamin, Slovenia) was used as a prepolymer for microcapsule wall. Styrene-maleic acid anhydride copolymer (SMA) with average mol. weight 350,000 (Hercules) was used as a modifying agent and emulsifier for *in situ* polymerisation. Analytical grade sodium hydroxide (Kemika, Croatia) and sodium metabisulphite $Na_2S_2O_5$ (BASF) were used for termination of the polymerisation reaction and removal of free formaldehyde from the suspension of microcapsules. Four paraffinic hydrocarbons with melting points 25 ^oC, 28 ^oC, 40 ^oC and 50^oC (AGS, Turkey and Rubitherm, Germany) were used as PCMs for microencapsulation.

The *in situ* polymerisation microencapsulation process, based on (Knez, 1995; Kukovic & Knez 1997), consisted of the following steps: (1) preparation of an aqueous solution of a modifying agent (SMA) and its partial neutralisation with sodium hydroxide or ammonia; (2) emulsification of PCM at a temperature above the melting point; (3) addition of amino-aldehyde prepolymers for wall formation; (4) induction of polycondensation by rising temperature to 70 - 80^oC; (5) polycondensation reaction at an elevated temperature, about 1 hour; (6) termination of polycondensation by raising pH to 7,0 and cooling to a room temperature; (7) removal of free formaldehyde in a reaction with ammonia or sodium metabisulphite. Aqueous suspensions of microencapsulated PCMs were dried by a Büchi B290 and NIRO pilot spray dryer.

The mechanical strength of PCM microcapsules was tested by a smudging colouration test, which was originally designed for pressure-sensitive copying papers. A leuco dye marker was incorporated in microcapsules, prepared by the same procedure as for PCMs, except that a 3% Crystal violet lactone leuco dye in KMC-113 diisopropyl naphthalene was used as a core material. Microcapsules were coated onto a paper sheet, over which a colour developer sheet was placed. Under the pressure of standardised weights (e.g. a 500 g weight of 5 cm in diameter), the upper paper was pulled away, and the intensity of coloured stains was evaluated, occurring as a result of the colour formation reaction between the leuco dye (leaking from mechanically ruptured microcapsules) and the colour developer.

Microcapsule diameter and size distribution were measurd by Alkatel Cilas Laser Granulometer 715. Olympus microscope BX60 with a Sony CEN50 camera was used for characterisation of visual appearance, individual microcapsule size and morphological characteristics of microcapsules. Scanning electron microscopy was performed by JEOL JSM-6060LV microscope, at accelerating voltage 15 kV, with microcapsule coating C + Au/Pd. The melting points of PCMs were determined by differential scanning calorimetry (Perkin Elmer Pyris-1).

Results and discussion

To remain functional over numerous phase transition cycles, microencapsulated PCMs have to remain encapsulated within the impermeable microcapsule walls for the whole product life. PCM microcapsules needed to be highly resistant to mechanical stress, which was achieved by modifications of the microencapsulation process. Better process control and improved mechanical properties of PCM microcapsules were achieved primarily by the selection and optimisation of a combination of wall prepolymer (partly methylated TMM) and the modifying agent (SMA copolymer with the molecular weight of 350.000 g/mol), which had a double function of being an emulsifier and a polycondensation initiator for melamine-formaldehyde precondensates. At optimum conditions, polymerisation evenly developed at the surface of the emulsified PCMs, thus forming an impermeable microcapsule wall.

The optimized process parameters for the microencapsulation of PCMs in a 10L reactor were as follows: filling 7 – 10 L; amount of PCM in the emulsion (microcapsule core) 25 – 40 %; concentration of the SMA modifying agent 4 – 6.5 %; concentration of partly methylated TMM (microcapsule wall prepolymer) 18,5 – 40 g/100 mL of microcapsule core material; dissolver stirrer diameter 90 mm; mixing speed 1000 – 2000 rpm. The characteristics of microcapsules containing PCMs as the core material are listed in Table 1.

Parameters	***Values***			
PCM melting point (^{o}C)	25	28	40	50
Mixing during O/W emulsification (rpm)	1500	1500	1900	1500
Average diameter of microcapsules (μm)	9.10	8.30	7.86	8.63
Average thickness of microcapsule wall (μm)	0.14	0.22	0.15	0.17
Microcapsule suspension pH	7.0	7.6	7.7	7.3
Microcapsule suspension viscosity at 25 ^{o}C, Brookfield (mPas)	300	425	300	470
Microcapsule suspension dry matter (%)	37.0	38.2	39.5	36.4

Table 1: Four batches of microcapsules containing PCMs with melting points of 25 ^{o}C, 28 ^{o}C, 40 ^{o}C and 50 ^{o}C

PCMs with a melting point of 25 ^{o}C and 28^{o}C were microencapsulated by *in situ* process without cooling, while for PCMs with higher melting points (40^{o}C and 50^{oC}) the microencapsulation procedure had to be modified. The first process modification was based on an additional cooling step, inserted between the emulsification of PCM and the addition of wall materials. Cooling prevented a premature uncontrolled polycondensation, causing irregular precipitation of wall polymers onto PCM cores in oil-in-water emulsion, consequently resulting in a lower quality of microcapsules. Introduction of a cooling step successfully prevented premature polycondensation, but exhibited some unexpected negative effects, such as an instability and collapse of the emulsion system. A possible reason for this phenomenon was a change in adsorption characteristics of the solid state PCM for the SMA emulsifier. In addition, changes of the aggregate state of emulsified PCM from liquid into a solid state and back into liquid during the consecutive polycondensation step caused volume changes (shrinking and expanding) of emulsified PCM droplets during the sensitive time of wall formation for up to 5 - 10 vol.%. These caused disturbances in wall formation.

As an alternative to cooling, the second process modification introduced a wall prepolymer dilution and its addition to a system at a temperature above the melting point of the PCM, at high speed stirring. TMM prepolymer was diluted to 30% of dry matter content. The premature polycondensation was avoided, and the resulting quality and mechanical resistance of microcapsules was good.

In tests of microencapsulation of PCMs by *in situ* polymerisation without cooling, effects were studied of the ratio between the modifying agent (SMA) and the wall material (TMM) on microcapsule size, wall permeability and mechanical resistance. The strength of microcapsule walls strongly depended on morphological properties of the microcapsule walls, especially on microcapsule wall thickness and porosity.

Experiments showed that the wall permeability and pore sizes depended on the ratio between the modifying agent (SMA) and the wall material (TMM). The higher the ratio, the thinner were the walls, the smaller were the pores in microcapsule walls, and the lower was the wall permeability (Table 2).

The optimised process enabled the production of microencapsulated hydrocarbon PCMs with mechanically and thermally stable amino-aldehyde walls (Figure 1). By regulating the ratio of entering raw materials, it was possible to change the properties of microcapsule walls, as well as to regulate the dry matter content, pH and viscosity of the final microcapsule suspensions.

Parameter	*Batch 1: larger microcapsules with thicker walls*	*Batch 2: Smaller microcapsules with thinner walls*
SMA : TMM ratio (g/g)	0.45	0.62
SMA : PCM ratio (g/g)	7.66 : 100	12.7 : 100
TMM : PCM ratio (g/g)	17.14 : 100	20.6 : 100
Emulsification	20 min, 1300 rpm	20 min, 1600 rpm
Wall hardening	60 min, 80°C	60 min, 80°C
Average microcapsule wall thickness (μm)	0.093	0.065
Average microcapsule diameter (μm)	5.91	2.78
Average microcapsule surface (m^2/g)	1.69	2.7
Average number of microcapsules per g of dry microcapsules (10^9)	352	453

Table 2: Comparison of *in situ* polymerisation process parameters for the production of PCM microcapsules at different SMA (modifying agent) : TMM (wall prepolymer) ratios

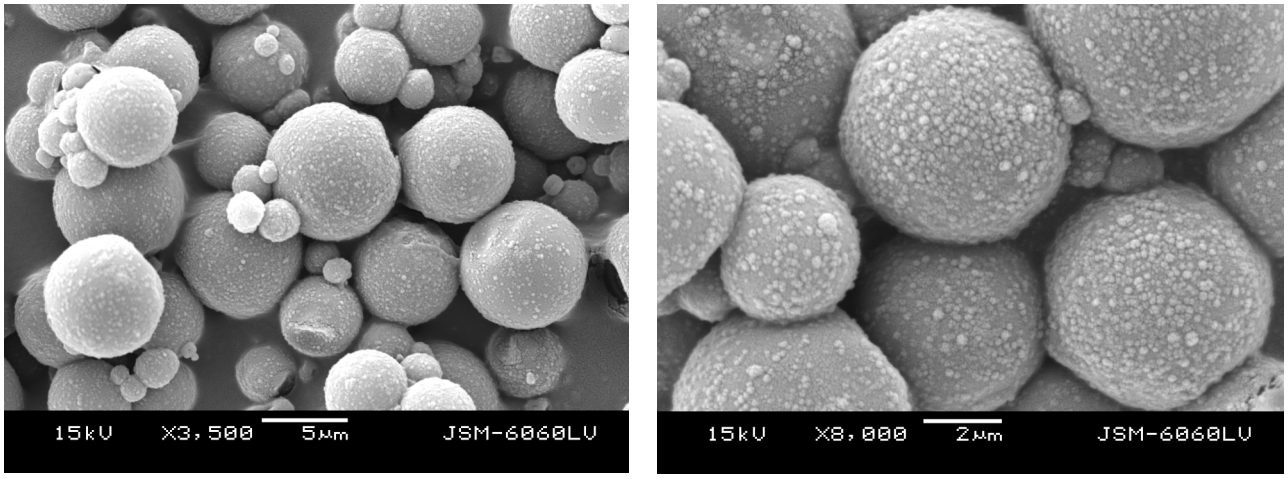

Figure 1: Scanning electron micrograph of microencapsules (3-6 μm in diameter) containing paraffinic PCMs, obtained after the spray drying of the microcapsule suspension, magnification 3.500 x (left) and 8000 x (right)

Conclusions

The work focussed on *in situ* polymerisation microencapsulation of PCMs, which are used in different applications for the active exchange of heat. In addition to impermeability, an improved mechanical resistance of microcapsule walls was needed, to assure a sufficient mechanical strength to withstand solid-liquid transitions of PCM in microcapsule core without leaking. Main process modifications to reach the desired microcapsule characteristics were based primarily on the selection and ratio of the melamine-aldehyde prepolymer (TMM) and of a modifying agent (SMA), as well as on the determination of emulsification and polymerisation parameters (rpm, temperature, duration). Experiments in a 10L reactor showed that for each core material, process parameters had to be empirically optimised to achieve the desired characteristics.

References

Knez, E. (1995) *Method for the production of microcapsules*, patent SI 8411319, Aero d.d.
Kukovič, M. & Knez E. (1997) *Process for preparing carriers saturated or coated with microencapsulated scents*, patent EP 0782475, Aero d.d.

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