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The Manufacture of Microencapsulated Thermal Energy Storage Compounds Suitable for Smart Textile

Salaün Fabien^{1,2}

¹Univ Lille Nord de France,

²ENSAIT, GEMTEX;

France

1. Introduction

Smart textiles are able to sense electrical, thermal, chemical, magnetic, or other stimuli from the environment and adapt or respond to them, using functionalities integrated into the textile structure. As an important consideration in active wear, clothing comfort is closely related to microclimate temperature and humidity between clothing and skin.

Since the end of the 80's, functional textiles have been developed to enhance textile performances according to the consumers' demand and to include a large range of properties with a higher added value. One of the possible ways to manufacture functional or intelligent textile products is the incorporation of microcapsules or the use of microencapsulation processes for textile finishing. Thermal storage by latent heat was early recognised as an attractive alternative to sensible heat storage to improve the thermal performance of clothing during the modifications of environmental temperature conditions. Early efforts in the development of latent heat storage used organic phase change materials (PCMs) for this purpose. PCMs are entrapped in a microcapsule of a few micrometers in diameter to protect them and to prevent their leakage during its liquid phase. In the two past decades, microencapsulated Phase Change Materials have drawn an increasing interest to provide enhanced thermal functionalities in a wide variety of applications. When the encapsulated PCMs is heated above its phase change temperature, it absorbs heat as it goes from a solid state to a liquid state or during a solid to solid transition. It can be applied to clothes technology, building insulation, energy storage as well as to coolant liquids. On a more general basis, it can be used to design a broad variety of thermal transient regimes. Recent research has investigated the incorporation of organic PCMs directly into the fabric fibers (Zhang et al. (2006)) or coated on the substrate surface (Choi et al. (2004), Shin et al. (2005)), creating functional and effective textile elements which can significantly affect thermal insulation. Moreover, thermal comfort sensation is closely related to microclimate temperature and humidity. Thus, Fan & Cheng (2005) denoted that a lower moisture absorption rate is beneficial to thermal comfort. Therefore, the thermal functional performance of a thermoregulated fabric is not only influenced by the latent heat of PCMs but also by the design of the textile structure.

2. Classification of heat storage materials to melting temperature range and textile application

Among the various heat storage technologies available, i.e. sensible heat based on increasing the temperature without changing the phase of the material, latent heat based on the transition of a material according to the temperature and thermo-chemical heat (or heat of reaction) based on the thermophysics of the reactions; thermal heat storage in the form of latent heat of phase change seems to be particularly attractive in textile fields. A variety of PCMs are well-known for their thermal characteristics relating to their phase change stage. These compounds possess the ability to absorb and store large amounts of latent heat during the heating process and release this energy during the cooling process. Thus, materials being converted from solid to liquid, from liquid to solid or solid 1 to solid 2 states are suitable to be used in the manufacture of thermoregulated textiles. The selection of a PCMs formulation depends typically on the required phase change temperature depending on end use. Indeed, PCMs should react to changes in temperature of both the body and the outer layer of the garment when they are incorporated in the textile substrate. Thus, for textile applications, PCMs with a phase change within the ambient temperature and comfort range of humans are suitable, i.e. in a temperature range from 15°C to 35°C.

Among the various ways to store energy, the most attractive form is latent heat storage in phase change material, because of the advantages of high storage capacity in a small volume and charging/discharging heat from the system at a nearly constant temperature (Abhat, 1983). Thermal storage by latent heat was recognised early as an attractive alternative to sensible heat storage to improve the thermal performance of clothing during the changes of environmental temperature conditions. The latent heat associated with a first-order phase transition provides a mechanism for the thermal energy storage. The phase changes comprise predominantly solid-liquid transitions for thermal storage applications in textiles. The use of PCMs is linked to its latent heat of fusion for thermal storage. The latent heat of fusion of a material is substantially greater than its sensible heat capacity. Stated differently, the amount of energy that a material absorbs upon melting or releases upon freezing is much greater than the amount of energy which it absorbs with a weak variation of temperature. Upon melting or freezing, a PCM absorbs and releases substantially more energy than a sensible heat storage material which is heated or cooled to the same temperature range. The storage capacity of PCMs (Q) equals the phase change and the sensible heat stored at the phase change temperature (1). Thus, the latent storage is always increased by a significant extent by their sensible storage capacity. Furthermore, during the complete phase change process, the temperature of the PCMs as well as the surrounding media remains nearly constant (Feldman et al., 1986).

$$Q = m \cdot \int_{T_{\text{initial}}}^{T_{\text{Tr}}} C_p(T) \cdot dT + m \cdot \Delta H + m \cdot \int_{T_{\text{Tr}}}^{T_{\text{end}}} C_p(T) \cdot dT \quad (1)$$

For a textile application, the following PCMs properties should be required, i.e. a high value of the heat of fusion and specific heat per unit volume and weight; a melting point in the application range (between 15°C to 35°C); a high thermal conductivity; a chemical stability and non-corrosiveness; PCMs should not be hazardous, non-flammable or poisonous; PCMs should have a reproducible crystallisation without decomposition; PCMs should present a small supercooling degree and high rate of crystal growth; they should have a small volume

variation during the phase change process; and PCMs should be sufficiently abundant at a low cost.

The most common PCMs, with a phase change temperature suitable for textile application, can be divided into two groups, i.e. organic compounds such as paraffins or linear alkyl hydrocarbon and non paraffinic materials (hydrocarbon alcohol, hydrocarbon acid, polyethylene or polytetramethylene glycol, aliphatic polyester...), and inorganic compounds such as hydrated inorganic salts, eutectics or polyhydric alcohol-water solution (Zhang, 2001).

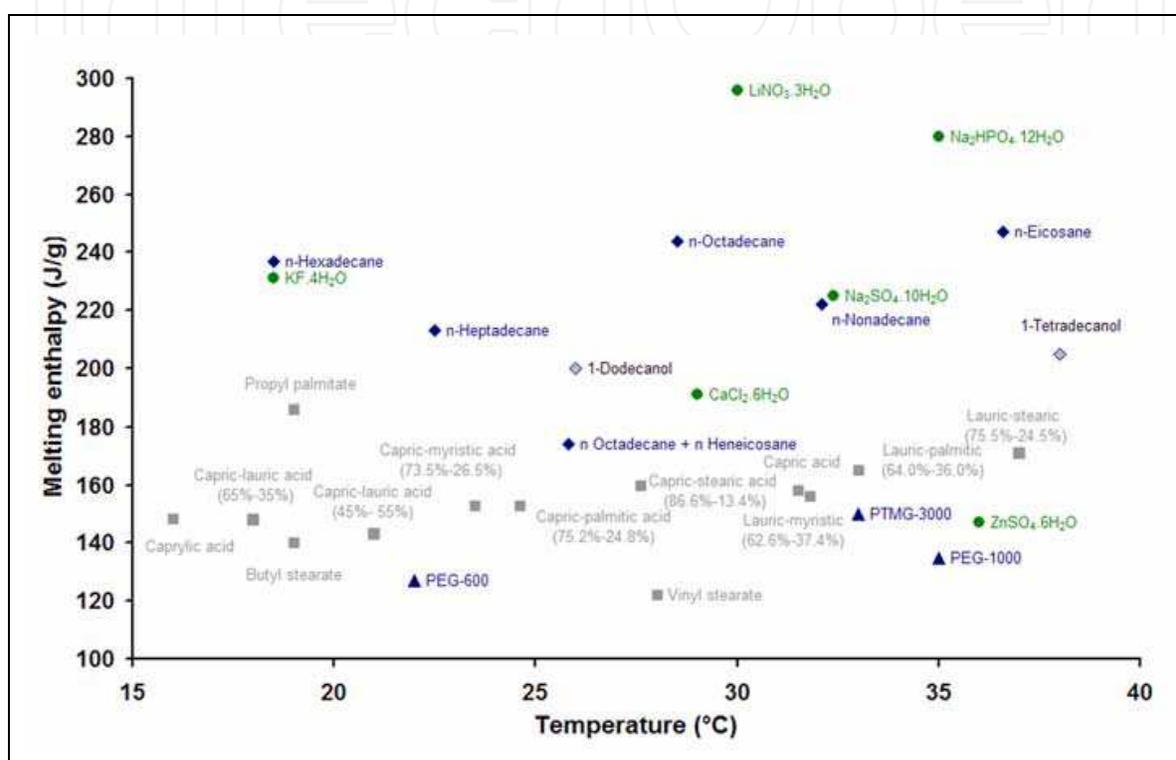


Fig. 1. Temperature ranges and corresponding melting enthalpy of suitable PCMs for textile applications

2.1 Organic phase change materials

Organic solid-liquid PCMs include paraffin, alkyl esters and acids, polyethylene glycol and its derivatives.

2.1.1 Polyhydric alcohols

Polyhydric alcohol, or plastic crystal, are solid-solid phase change materials, and even if they are not suitable for textile application since their phase change temperature is higher than the upper end-use limit, they present small volume change, lower undercooling, no phase separation and no leakage. Amongst them, pentaerythritol ($C(CH_2OH)_4$), trimethylol ethane ($((CH_3)C(CH_2OH)_3$), neopentyl glycol ($((CH_3)_2C(CH_2OH)_2$), their NH_2 -substituted compounds and 2-amino-2-methyl-1,3-propanediol ($((CH_2CH_2OH)_2CCH_3NH_2$), 2-amino-2-hydroxymethyl-1,3-propanediol ($((CH_2CH_2OH)_3CNH_2$), and their binary mixtures have an endothermic or exothermic effect under their melting point and are cited as potential candidate for thermal energy storage. Furthermore, the phase change temperatures and heat

of binary mixture of polyhydric alcohol are lower than of the raw material. Thus, Wang et al. have found that the phase change of neopentylglycol/pentaerythritol and trihydroxy methylaminomethane were between 30 and 40°C (Wang et al., 2000).

2.1.2 Polyethylene glycols

In the field of organic PCMs, polyethylene glycols (PEGs) $(-O-CH_2-CH_2)_n$ and their derivatives, such as poly(tetra methylene glycol) (PTMG), have been widely used as solid-liquid thermal energy storage materials since they present high transition enthalpy depending on their molecular weight, congruent melting behaviour, wide range of transition temperature to obtain suitable melting point, in contrast to inorganic compounds. Furthermore, their melting points and enthalpies depend on their molecular weight. Thus, PEGs with a molecular weight comprised between 600 and 1500 g.mol⁻¹ have melting points in the temperature range between 17°C to 35°C and a melting enthalpy between 120 to 140 J.g⁻¹. The use of PTMG as phase change material in textile field is limited due to a supercooling phenomena even if the PTMG 3000 show a melting point about 33°C for a melting enthalpy about 150 J.g⁻¹.

Furthermore, great efforts were made to prepare new PEG solid-solid PCMs with another compound to keep the material in solid state during the phase change; and thus prevent its leakage. Nevertheless, these compounds lose their thermal properties after several heating-cooling cycles.

2.1.3 Linear chain hydrocarbons

Linear hydrocarbons, C_nH_{2n+2} , with a melting temperature between 16°C to 38°C, are the most common PCMs used for textiles. Thus, *n*-alkanes were preferred due to their high latent heat, and they are chemically inert, non-toxic, non-corrosive and non-hygroscopic. Thus, *n*-eicosane (Sarier & Onder, 2007a), *n*-octadecane (Pause, 2001; Shim et al., 2001; Choi et al., 2004; Li & Zhu, 2004; Chung & Cho, 2004; Zhang et al., 2005b, 2006; Sarier & Onder, 2007a, 2007b) and *n*-hexadecane (Shim et al., 2001; Sarier & Onder, 2007a, 2007b) are the most PCMs chosen to be applied. In these studies, pure compound was used as PCM material and therefore the phase change occurs in a narrow temperature change at the melting temperature of the *n*-alkane. The use of binary mixture of *n*-alkanes allows to adjust the melting point (or phase change temperature) by modifying the composition, that also leads to a decrease in the overall latent heat of fusion (Kumano et al., 2005). Furthermore, some of the binary mixture, i.e. *n*-hexadecane/ *n*-octadecane (Métivaud, 1999), *n*-octadecane/ *n*-hexadecane (Métivaud, 1999), or *n*-tetradecane/ *n*-hexadecane (Bo et al., 1999) have a solid/liquid or a solid/solid transition which takes place in a relatively narrow temperature range. The use of the binary mixture of *n*-hexadecane/ *n*-eicosane allows to widen this temperature change and can be suitable for textiles application (Salaün et al., 2008a, 2010a). Nevertheless, this widening is accompanied by a decrease of the latent heat which can be caused by the formation of a concentration distribution in the liquid film due to small scale segregation (Kumano et al., 2005). The binary mixture of *n*-hexadecane/ *n*-eicosane was also studied by Sarier et al., they concluded that to enhance the thermal capacity of fabrics, it should be better to use a combination of microcapsules containing different types of PCMs rather than those including a mixture of them (Sarier & Onder, 2007a). They have observed that the mixture was satisfactory to provide a buffering effect against temperature changes and to regulate the temperature at the target of desired value.

2.1.4 Fatty acids

Fatty acids are friendly PCMs and show several advantages such as a high phase change enthalpy, congruent melting and freezing behaviour and good chemical and thermal stability. Even if capric, lauric, myristic, palmitic or stearic acids have good thermal and heat transfer characteristics, their melting points between to 32°C to 61°C are quite high for textile energy storage (Feldman et al., 1989; Sari, 2003). Nevertheless, the eutectics of capric-lauric, capric-palmitic, lauric-myristic, lauric-palmitic, and lauric-stearic binary mixture, with melting points of 18.0, 21.8, 32.7, 34.2 and 34°C, and heats of melting of 120, 171, 150, 167 and 160 J.g⁻¹, respectively seem to be suitable PCMs for textile applications (Sari, 2005; Sari & Karaipekli, 2008).

Zeng et al. have analyzed the thermal properties of a binary mixture of palmitic acid and 1-tetradecanol. The eutectic composition mixture (point at 29°C and melting enthalpy of 143 J.g⁻¹) could be viewed as a new phase change material with large thermal energy storage capacity (Zeng et al., 2009).

Although, the thermal properties of fatty acid ester were few studied, these compounds show a solid-liquid phase transition within a narrow temperature range, which should be promising for thermal energy storage (Li & Ding, 2007a, 2007b; Alkan et al., 2008; Sari et al., 2009a). Thus, for isopropyl stearate, butyl stearate, and vinyl stearate and, the thermal characteristics determined by Feldman et al. are as follow : melting point : 14, 19, and 27°C , respectively and the melting enthalpy range from 120 to 142 J.g⁻¹ (Feldman et al., 1986; Feldman et al., 1995).

2.2 Hydrated inorganic salts

Hydrated inorganic salts, e.g. salt with 'n' water molecules, are attractive materials with their relatively high latent heat per unit weight (from 150 to 300 J.g⁻¹), high thermal conductivity (~0.5 W.M⁻¹.K⁻¹), non flammability property and moderate costs. Nevertheless, their use is mainly limited by their incongruent melting, supercooling behaviour when there are incorporated in the textile substrate, which can occur after several phase change cycle. If LiNO₃.3H₂O is stable during at least 25 cycles, phase segregation of CaCl₂.6H₂O or Na₂SO₄.10H₂O should be observed after only few cycles. Thus, it was suggested to overcome these problems to use an extra water amount to limit the formation of heavy anhydrous salt, which results in the reduction of the storage density (Salaün et al., 2010b; Biswas, 1977). The use of thickening to overcome phase segregation, such as betonite, or nucleating agent to limit the supercooling phenomena, have also be suggested, but in all cases the thermal properties of the inorganic PCMs are reduced. Furthermore, when inorganic PCMs are encapsulated, the process as well as the morphology of the resulting capsules affects the thermal properties of the materials (Salaün et al., 2010b).

2.3 Conclusion

Many substances have been studied as potential PCMs with regard to their typical range of melting and melting enthalpy, within the human comfort range of 18°C to 35°C. This kind of materials absorbs and emits heat while maintaining a nearly constant temperature, and thus they are very effective since they can store 5 to 14 times more heat per unit volume than sensible storage materials. Each type of PCMs presents some advantages or disadvantages. On the one hand, organic PCMs have excellent stability concerning the thermal cycling, but they are flammable and their melting enthalpy and storage density are relatively low

compared to salt hydrates. On the other hand, the main problem with inorganic PCMs are their corrosiveness, their cycling stability and the existence of a subcooling phenomena which be reduced by adding into the materials some nucleating agents.

3. Microencapsulation

For a textile use, PCMs should be surrounded by a protective shell to avoid any liquid migration during the phase change step and therefore to preserve PCMs in the polymer shell as long as possible through the heating/cooling cycles. Besides, the encapsulation step allows to increase the heat transfer area, to decrease the reactivity of the core materials, to limit the interference with other materials parameters, to enhance the low heat conductivity and the manipulation of PCMs becomes easier. Microencapsulated PCMs have attracted more and more attention since the end of the 1980s (Kaska & Chen, 1985; Bryant & Colvin, 1988). It was progressively established as an interesting alternative to the traditional materials where the imprisoned air was the principal insulating element. The choice of the polymer for the membrane synthesis of the microcapsules is linked to the considered application and the required material processes. In the textile field, the polymers used should have good thermomechanical properties to resist to the thermal and mechanical requests during of the implementation processes, and during the daily use by the wearer. The use of microencapsulated phase change material in textile requires a high thermal stability of these particles that is influenced by the shell and the core materials. A review on the various techniques available for the microencapsulation of Phase Change Materials is presented. The methods can be classified as being either physical or chemical based.

3.1 Principle and generalities

Microencapsulation refers to the formation of polymeric particles with a range of diameters from nanometers to millimeters, and which exhibits several kinds of morphologies, in which the mains are so called microcapsules and microspheres (Benita, 1996). Microspheres consist of polymeric network structure in which an active substance is enclosed, whereas in microcapsules or core/shell structures exhibit a reservoir structure, i.e. the core substance is surrounded by a polymeric layer. Even if, microencapsulation principle was firstly introduced by Green and Schleicher in the 1950s to create microcapsules for carbonless copying paper (Green & Schleicher, 1956 a & b, as cited in Arshady, 1990), textile applications were mainly developed in labs since the early 1990's and actually we can see much more applications in the textile industry for developing new properties and added values (Nelson, 2002).

Although, there are more than 200 microencapsulation methods described in scientific literature and patent, most of them include three basic steps, i.e. enclosure of core component, formation of the microparticles, and hardening of it. These methods are generally divided or classified in three main groups, which are based on the mechanisms of microparticle formation, such as mechanical, chemical and physico-chemical processes. The choice of a method rather than another is based on the cost of processing, the use of organic solvents for health and environment considerations. Nevertheless, the microencapsulation processes used in textile industry are generally focused on chemical and physico-chemical methods, because mechanical processes lead to the formation of particles with a mean diameter higher than 100 μm . Even if microparticles with mean size distribution in the range of 20 to 40 μm should be useful for textile application (Nelson, 2001), very small

microparticles (mean diameter ranging from 1 to 10 μm) are preferably incorporated within textile fibers (Cox, 1998; Bryant, 1999) but according to Colvin (Colvin, 2000) particles with a mean diameter less than 1 μm are suitable for fiber fabrication; and larger microcapsules (mean diameter up to 100 μm) should be used into foams or coated formulation (Colvin & Bryant, 1996; Pushaw, 1997).

Therefore, the most suitable methods include interfacial, *in-situ* and suspension polymerization methods for chemical processes and simple or complex phase coacervation for physico-chemical processes, and spray drying for the mechanical processes (Borreguero et al., 2011; Hawlader et al., 2000 & 2003; Teixeira et al., 2004). In all cases, the microencapsulation process includes two main steps, e.g. emulsification step which determines the size and the size distribution of the microcapsules; and the formation of the capsules. The emulsification step may be influenced at once by physical parameters such as apparatus configuration, stirring rate and volume ratio of the two phases, and by physicochemical properties such as interfacial tension, viscosities, densities and the chemical compositions of the two phases. The formation of microcapsules is greatly affected by the surfactant, which influences not only the mean diameter but also the stability of the dispersion. The surfactants used in the system have two roles, one to reduce the interfacial tension between oil and aqueous phases allowing formation of smaller microcapsules and one to prevent coalescence by its adsorption on the oil-water interface and therefore by forming a layer around the oil droplets. The second step, or the synthesis of a core/shell particle or other possible morphologies, is mainly governed by the kinetic factors, i.e. the ability of the monomers, pre-polymer or polymer to react or to cross-link, and thermodynamic factors, i.e. the minimum total free energy exchange in the system. The spreading coefficient should be used to predict the engulfment of PCMs within polymer in a continuous immiscible phase (Torza & Mason, 1970; Sundberg & Sundberg, 1993, Loxley & Vincent, 1998; Sánchez et al., 2007; Salaün et al., 2008a).

3.2 State of the art in microencapsulated PCM's

The microencapsulation of phase change materials has been widely investigated since the late 1970s to provide significantly enhanced thermal management for various application fields. Thus, preliminary work on microencapsulation of phase change materials was begun at General Electric under the sponsorship of the U.S Department of Energy. This was the first such attempt and was directed toward the development of a two-component heat transfer fluid for use in solar systems for residential applications (Colvin & Mulligan, 1986).

The microencapsulation of PCMs provides some benefit effects on the heat storage, since the shape of the storage material is arbitrary, temperature gradient is more favourable and PCMs lifetime increases. Furthermore, the product is always in a dried state since the phase change occurs within the coating material. The microcapsules' embedment in heat storage is relatively simple, and the various PCMs formulation with different melting temperatures should be used to obtain the desired temperature in which phase change occurs. The use of microcapsules increase the specific exchange area, which is provided for effective heat transfer; and thus large quantities of thermal energy can be stored and released at a relatively constant temperature without significant volume change since in the particles, the size remains constant and sufficient space or free volume exist. Finally, the encapsulation step allows to reduce or to avoid problems as such supercooling and phase separation (Hawlader et al., 2003). Therefore, to maintain the reversibility of the PCMs

functionality, they are encapsulated within the impermeable microcapsules walls for the whole product life. Furthermore, the microcapsules need to be resistant to mechanical and thermal stresses.

The PCMs, having a phase change temperature between -10 and 80°C , can be used for encapsulation (Jahns). Furthermore, according Lane, over 200 phase change materials, with a melting point from 10 to 90°C , are suitable to be encapsulated (Lane, 1980). Thus, among all the potential PCMs used to be microencapsulated in a polyester resin, the best results were obtained by using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. From this study, various encapsulation strategies have been explored to entrap inorganic compounds, since the organic PCMs tested migrated into the polymer encapsulant and the thermal cycling stability was poor due to leakage problem after 100 thermal cycle test runs, link to the thickness of the polymeric shell (Roy & Sengupta, 1991) and to the mean size (Colvin & Mulligan, 1986). Thus, up to the 1990s, few reports have been published on the microencapsulation of paraffin. Even if a primary use of the mPCMs products is for the textile industry, mPCMs are also finding wide spread applications in others areas such as electronic for cooling electrical component, as building materials to increase the energy efficiency of building, or as storage solution for packaging and agriculture to thermally protect products. Thus, since the middle of the 1990s, there has been a renewed interest in using mPCMs to enhance performance of fluid convective heat transfer (Yamagishi et al., 1999) or gas fluidised bed (Brown et al., 1998), textile (Bryant & Colvin, 1988 & 1996; Cox, 1998; Pause, 1994 & 1995), building material and also solar energy system (Hawllader et al., 2003).

However, at the current state of microencapsulation technology, most of commercial textile application of PCM choice is restricted to paraffins or organic compounds (Mehling & Cabeza, 2008); and these compounds are available as slurry or fluid dispersion and dried powder. Nevertheless, Salaün et al. (2008b & 2010b) have tried to encapsulate hydrated salt.

3.3 Microencapsulation methods

One of the most typical methods which may be used to microencapsulate a PCM is to disperse droplets of this molten material in an aqueous solution and to form walls around the droplets. A literature survey on mPCMS indicates that the most suitable methods include interfacial, *in-situ* and suspension polymerization methods for chemical processes and simple or complex phase coacervation for physico-chemical processes and spray-drying for the mechanical processes.

The choice of the shell materials has been widely investigated by several researchers (Table 1) to enhance the structural anti-permeability or to bring up a solid protection and to improve the thermal stability of these particles. The selection of the microencapsulation process is mainly governed by the choice of the chemical nature of shell materials and by the desired mean diameter. Thus, the *in situ* polymerization is suitable for the melamine derivatives, the interfacial polymerizations were used to obtain polyurea and polyurethane walls, whereas PMMA and styrenic shells were obtained from emulsion polymerization and suspension-like polymerization reactions, respectively. The use of hydrosoluble polymers imply to select a coacervation or a spray-drying method. Furthermore, since a few years, a new process based on a sol-gel or core templating was used to obtain silica shell. Besides, microencapsulation of PCMs is essentially restricted to organic phase change materials, indeed the process technology does not allow to obtain a polymeric shell sufficiently tightened to prevent the small water molecules diffusion during the phase changes of the salt hydrate.

Table 1. Shell composition and some properties of microcapsules suitable for thermal heat storage

Microcapsule shell	Core material	Encapsulation ratio	Microcapsule diameter	Melting temperature	Latent heat of melting	Me
		wt. %	μm	$^{\circ}\text{C}$	$\text{J}\cdot\text{g}^{-1}$	
Polyurea	<i>n</i> -Hexadecane	28.0	2.5	15.5	66.1	Interfacial p
Polyurea	Butyl stearate	66.0	20-35	28.6	76.3	Interfacial p
Polyurea	<i>n</i> -Octadecane	26.0-46.4	0.1-1	29.5-30.8	53.6-110.0	interfacial p
Polyurea	<i>n</i> -Octadecane	70.0-75.0	7-16	26.8-28.2	153.2-188.9	interfacial p
Polyurea	<i>n</i> -Eicosane	75.0	2-6	35.7	55.5	Interfacial p
Polyurethane	<i>n</i> -Octadecane	40.0-70.0	5-10	~29.5-30.5	110.0-117.5	Interfacial p
Melamine-formaldehyde	<i>n</i> -Hexadecane	67.2	2	16.4	160.0	In situ pol
Melamine-formaldehyde	<i>n</i> -Octadecane	59.0	2.2	40.6	144.0	In situ pol
Melamine-formaldehyde	<i>n</i> -Octadecane	70.0	9.2	30.5	169.0	In situ pol
Melamine-formaldehyde	<i>n</i> -Octadecane	40.0	1.3	---	166.0	In situ pol
Melamine-formaldehyde	<i>n</i> -Octadecane	74.0	2-10	27.0	167.0	In situ pol
Melamine-formaldehyde	<i>n</i> -Octadecane	---	3-5	28.6	153.7	In situ pol
Melamine-formaldehyde	<i>n</i> -Octadecane	---	1-1.5	28.0	141.0	In situ pol
Melamine-formaldehyde	Lauryl alcohol	75.0	9.2	---	---	In situ pol
Melamine-formaldehyde	<i>n</i> -Hexadecane/ <i>n</i> -Eicosane/ TOES (48/48/4)	77.0	1-2	15.1	173.1	In situ pol
Urea-melamine-formaldehyde	<i>n</i> -Octadecane	71.4-78.8	0.2-5.6	33.23-35.15	172.7-190.6	in situ pol
Urea-melamine-formaldehyde	<i>n</i> -Octadecane	72.0	0.3-6.4	36.5	167.0	In situ pol
Urea-melamine-formaldehyde	<i>n</i> -Nonadecane	69.0	---	30.3	233.0	In situ pol
Urea-melamine-formaldehyde	<i>n</i> -Eicosane	71.0	---	45.3	172.0	In situ pol

Table 1. (continues) Shell composition and some properties of microcapsules suitable for thermal heat storage

Microcapsule shell	Core material	Encapsulation ratio	Microcapsule diameter	Melting temperature	Latent heat of melting	Me
Melamine-formaldehyde/PVA-MDI	<i>n</i> -Hexadecane / Na ₂ HPO ₄ ·12H ₂ O	76.4	5-10	16.1	174.6	In interfacial p
Melamine-formaldehyde/PVA-MDI	<i>n</i> -Eicosane / Na ₂ HPO ₄ ·12H ₂ O	71.7	5-10	35.1	176.0	In interfacial p
Melamine-formaldehyde-resorcinol	<i>n</i> -Octadecane	75.0	12.3	26.9	146.5	in situ pol
Polymethylmethacrylate	<i>n</i> -Docosane	28.0	0.16	41.0	54.6	Emulsion p
Polymethylmethacrylate	<i>n</i> -Eicosane	35.0	0.7	35.2	84.2	Emulsion p
Polymethylmethacrylate	<i>n</i> -Octacosane	43.0	0.25	50.6	86.4	Emulsion p
Polymethylmethacrylate	<i>n</i> -Heptadecane	38.0	0.26	18.2	81.5	Emulsion p
Polymethylmethacrylate	Paraffin	61.2	0.5-2	24.0-33.0	101.0	Emulsion p
Styrene-methyl methacrylate copolymer	PRS® paraffin wax	43.1	380	41.8	87.5	Suspen polymerisa
Polystyrene	PRS® paraffin wax	20.5	38	35.2	41.6	Suspen polymerisa
Polystyrene	<i>n</i> -Nonadecane	49.3	10.5	---	119.8	Suspen polymerisa
Polystyrene	<i>n</i> -Octadecane	53.5	0.100-0.123	---	124.4	Suspen polymerisa
cross-linked PVA	<i>n</i> -Eicosane	70.0-85.0	50-250	43.4	218.7	
Gelatin	paraffin wax	---	500	---	56.0-58.0	Simple C
Gelatin-arabic gum	paraffin wax	33.3-66.6	50-100	---	28.4-85.9	Complex
Gelatin-arabic gum	paraffin wax	33.3-66.6	~1		193.3-239.8	Complex
Gelatin-arabic gum	PCM RT 27	49.0	9	25.2	79.0	Complex
Agar-Agar/arabic gum	PCM RT 27	48.0	12	26.4	78.0	Complex

3.3.1 Phase coacervation

Phase coacervation is one of the oldest and most widely used technique of microencapsulation, and can be divided into two groups, i.e. simple coacervation which implies the use of one colloidal solute such as gelatin (Uddin et al., 2002), and complex coacervation, in which the aqueous polymeric solution is prepared from the interaction of two oppositely charged colloids, such as gelatine-arabic gum (Hawllader et al., 2003; Onder et al., 2008) or silk fibroin chitosan (Deveci & Bassal, 2009). Coacervation can be defined as the separation of a macromolecular solution into two immiscible liquid phases, i.e. a dense coacervate phase and a dilute equilibrium phase. The general outline of this method consists in three consecutive steps carried out under agitation (Figure 2).

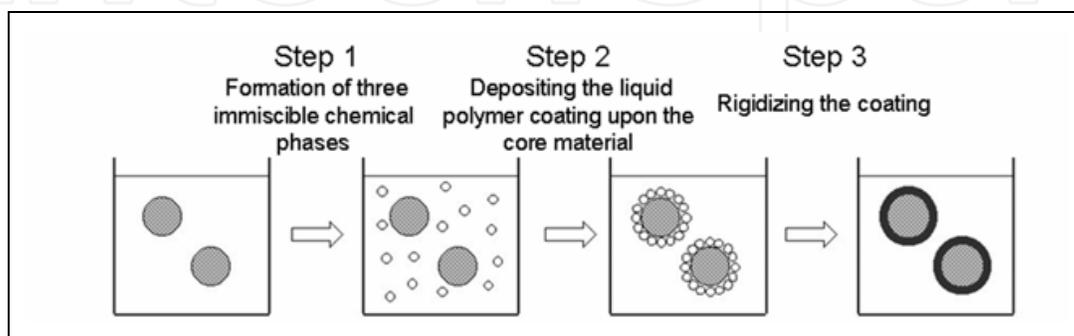


Fig. 2. Schematic representation of the various stages of the microencapsulation process by the coacervation method

Firstly, the core PCMs material is dispersed in an aqueous solution containing the coating polymer. Secondly, the deposition of the coating material is promoted by a reduction in the total free interfacial energy of the system, brought by the decrease of the coating material surface area during coalescence of the liquid polymer droplets. And thirdly, rigidizing of the coating material by thermal, cross linking or desolvation techniques is done to obtain solid particle.

The use of simple coacervation method was conducted by Uddin et al. (2002) to prepare microencapsulated paraffin. The aim of this study was to investigate the thermal performance of their microcapsules when they are subjected to cyclic operation. Thus, they reported that the microencapsulated paraffin has shown an energy storage and release capacity about 56-58 J.g⁻¹ during its phase change and this even after 1000 thermal cycles.

The complex coacervation method implies the use of two polyelectrolytes of opposite charges, i.e. gelatine/arabic gum (or acacia), agar-agar/Arabic gum or chitosan/silk fibroin. Thus, for the couple gelatine/gum Arabic, at pH<4.7, the gelatine is cationic, and gum Arabic is anionic. For example, as for the simple coacervation phase, the core material is initially dispersed in the gelatine solution at 40-60°C. To this dispersion, a solution of gum Arabic is added, and the pH is adjusted to ~4.0. This causes a liquid complex coacervate of gelatine-arabic gum and water to form, which surrounds the core to form primary capsules shell. The system is then cooled to room temperature to form the shell. The shell is then cross-linked by addition of glutaraldehyde or formaldehyde to react with amino groups on the chains. After adjusting the pH to 9-11 with NaOH solution, the solution is cooled down to 5-10°C during 2 to 4 hours.

Thus, Onder et al. (2008) have succeeded in the encapsulation of three paraffin waxes, namely *n*-hexadecane, *n*-octadecane and *n*-nonadecane by complex coacervation based on gelatin/arabic gum interactions before their incorporation into woven fabrics by coating.

They also found that the absorbed levels of coacervates were proportionnal with those of PCMs, and tended to increase when the dispersed PCM contents in emulsions were higher. Thus, the coacervates corresponding to 80 percent of *n*-hexadecane and *n*-octadecane addition, provided significant enthalpy, i.e. 144.7 and 165.8 J.g⁻¹, respectively.

3.3.2 Interfacial polycondensation

The microencapsulation of organic PCMs by interfacial polycondensation or polymerization involves the dispersion of the liposoluble phase in an aqueous continuous phase to induce the precipitation of the polymeric materials at the droplet interface. Each phase contains a dissolved specific monomer suitable to react with the other present in the other phase. The dispersed phase is as a good solvent for the monomers but acts as a non-solvent for the produced polymer. Therefore during polymerization, the system is composed of three mutually immiscible phases. Once, the various monomers were added to the system the reactions occur at the interface resulting in the formation of insoluble oligomers in the droplet, with tend to precipitate at the interface to form primary shell around the droplets. Further crosslinking reactions lead to the formation of growing shell by diffusion of monomers. When multifunctional monomers are used, a three-dimensional cross-linked system is obtained. Nevertheless, the thickness of the shell increases slowly due to the restricted diffusion of the starting monomers inducing layer morphology changes. The porosity of the capsules increases with the precipitation of the polymer at the interface and the solvent molecule diffusion through the wall. Furthermore, the main drawback of this method is the use of organic solvent, e.g. cyclohexane, to solubilize both core material and reactive liposoluble monomer. Based on this methods, polyurea, polyurethane, polyamide and polyester microcapsule shells should be prepared. For polyurethane or polyurea networks prepared from isocyanate and diols or diamine, the reaction of isocyanate groups with water molecules was promoted during the shell formation process. Furthermore, Cho et al. (2002) have observed that the formation of a polyurethane shell should be also provided from the reaction of the isocyanate with the hydroxyl groupments of the surfactant.

Su et al. (2007) have successfully synthetized a series of PU-shell microPCMs containing *n*-octadecane, their FTIR results have confirmed that the polyurethane shell was obtained form the reaction provided between TDI and DETA with SMA as a dispersant. The surface of the resulted microcapsules was observed as mostly smooth, and the shape was regularly spherical with a diameter of about 5-10 μm.

For the most reference cited in Table 1, toluene 2,4 diisocyanate was used as liposoluble monomer in cyclohexane or acetone, and three amino monomer were tested, i.e. ethylene diamine, tetraethylene diamine and Jeffamine T403 to obtain a polyurea shell. It was also found that the efficiency of *n*-alkane encapsulation increased as the core content decreased. Nevertheless, it is possible to reach narrow size distribution and high loading content, up to 70 wt.%.

3.3.3 In situ polymerization

Until now, melamine-formaldehyde and urea-formaldehyde resins were usually used or selected as microcapsule wall materials for the PCMs protection and also to improve the thermal stability of these particles. The use of this prepolymer offers some advantages to succeed in the synthesis of microcapsules due to their high reactivity, and therefore a short reaction time and a controlled amount of polymer to form the particles shell with a high loading content.

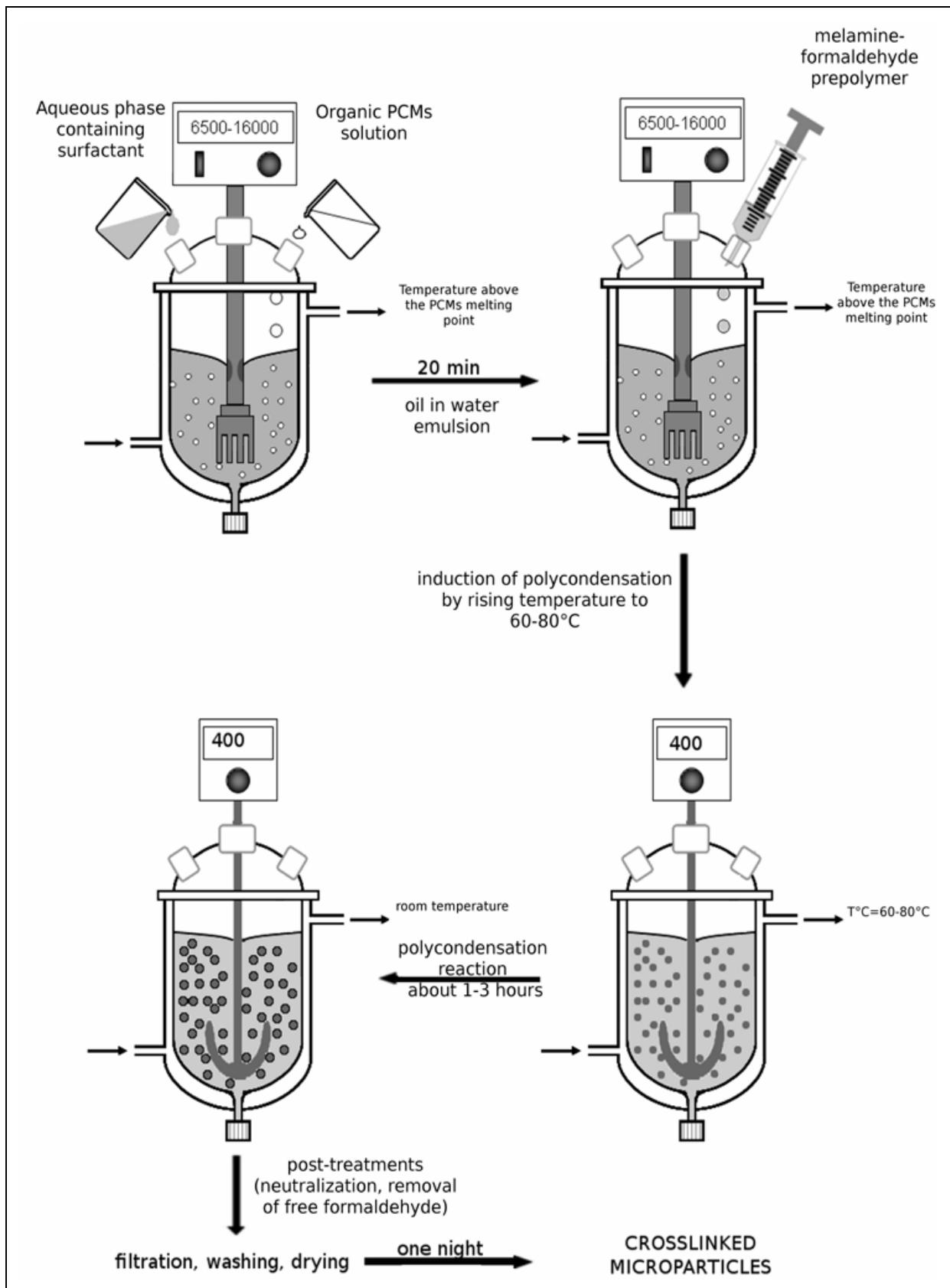


Fig. 3. Schematic representation of the various stages of the microencapsulation process by in situ polymerization

The *in situ* polymerization microencapsulation process, described in Fig. 3, consisted in the following steps: preparation of an oil in water emulsion from the dispersion of a PCMs melted solution in an aqueous continuous phase containing surfactant under high stirring rate; addition of melamine-formaldehyde pre-polymer for shell formation; induction of polycondensation by rising temperature to 60-80°C and/or by adjusting the pH of the emulsion to 4; when the desired size distribution was obtained, the stirring speed was decreased and polymerization occurred during 1 to 3 hours according to the temperature choice with continuous agitation; then the solution was cooled to room temperature, and neutralized, free formaldehyde was removed by adding ammonia. The suspension was then filtered, and the microcapsules were washed twice with methanol and distilled water.

This microencapsulation methods can start either from monomers, (i.e. melamine and formaldehyde, urea and formaldehyde or urea, melamine and formaldehyde), or from commercial prepolymers as such partially methylated trimethylmelamine, hexamethoxymethylolmelamine... (Šumiga et al., 2011). In all of these cases, the ability of amino resins for self condensation around the core material droplet is linked to its surface activity and is an enrichment of resin molecules within the interface. The reaction scheme for the synthesis was given in Fig. 4.

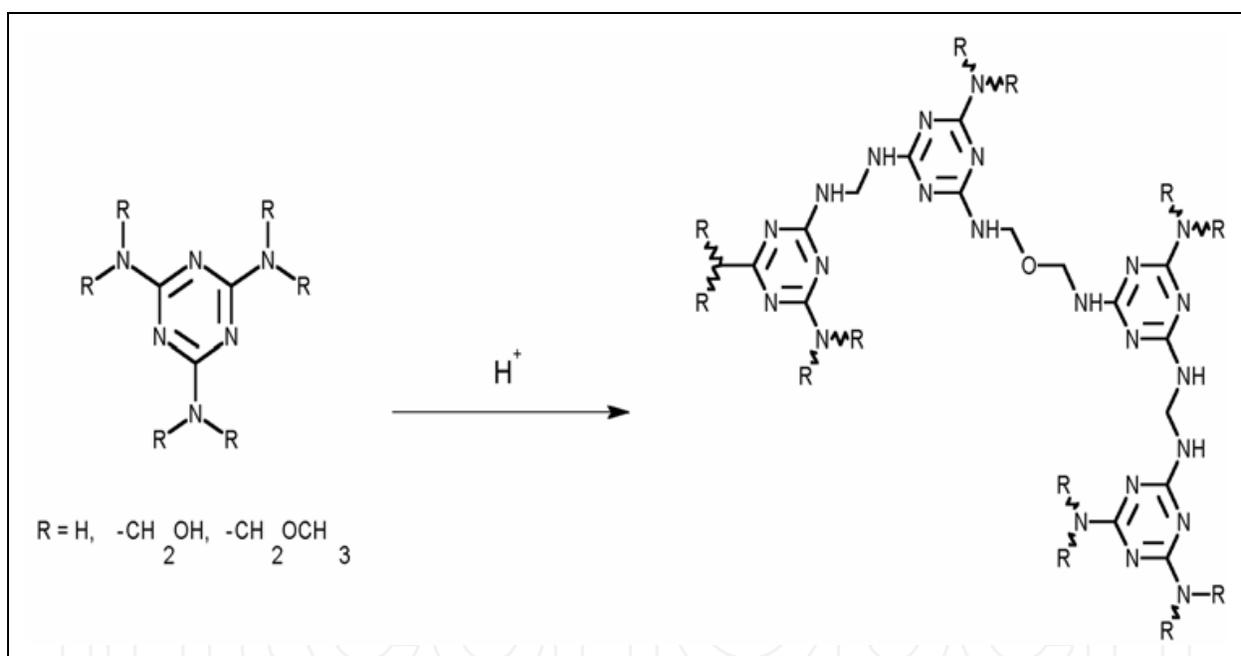


Fig. 4. Formation of cross-linked amino resin shell

The formation of the microcapsule shell described in the literature shows that it occurs in three consecutive stages (Salaün et al., 2009b). In the first step, the melamine-formaldehyde pre-polymers obtain H^+ changing into active pre-polymers under acidic condition, which results in an increase of the etherification degree due to a reduction in hydroxyl group concentration. Then, the water solubility of the pre-polymer decreases and the material separates from the continuous phase as a liquid solution relatively concentrated in active pre-polymer. During the second step, the amino resins wet the PCMs droplets to create primary shell around them. The concentration of resin in the boundary layer is enhanced by the hydrophilic/hydrophobic interactions of the partial methylolated melamine, and

therefore by an enrichment of resin molecules within the interface. Thus, the resin condensation proceeds much faster in the boundary layer than in the volume phase, allowing the formation of tougher capsule walls. From this step, it is possible to recover particle under powder form, nevertheless the capsule walls are not yet thermo-mechanically stable and not completely harden, and the particles should collapse during drying. In the last step the reaction rate of the polycondensation at the interface is increased with the result of microcapsule shell formation. During the polycondensation process, the particle surface becomes more and more hydrophobic, and according to the pH level, the shell is crosslinked either by ether linkage or methylene as shown in Fig. 4. Furthermore, the surface morphology depends mainly on the pH value, thus, a low pH value promotes the formation of methylene bridges affecting the amino resin solubility and therefore the obtention of a rough surface. The formation of higher oligomers of melamine-formaldehyde polymer with the formation of methylene bridges can be described as the reaction of bound CH_2OH group with H.

The use of an in situ method to prepare PCMs microcapsules results in a high loading content (from 60 to 80 wt.%) and a narrow size distribution (Table 1.); nevertheless the weight ratio of the core/shell materials affected also the particle size, its distribution and the surface morphology of the microcapsules (Salaün et al., 2009b). These particles have better thermal and mechanical stability properties than those synthesized from other polymers (Song et al., 2007). To improve their toughness, resorcinol can be added to the system (Zang & Wang, 2009b). However, the presence of free-formaldehyde after forming the shell may cause environmental and health problem; and it is relatively difficult to eliminate all formaldehyde which can be continuously released from the resultant microcapsules. To solve this problem, Li et al. (2007) have proposed to incorporate formaldehyde once and urea or melamine for three times; on the other hand, Šumiga et al. (2011) have observed that the use of ammonia during the post-treatment process allowed to decrease formaldehyde content level in the suspension.

3.3.4 Other microencapsulation methods

For several years, research on microencapsulation process has been focussed on new processes, either to obtain environmentally friendly products or to develop an easier, cheaper and robust method, such as suspension-like polymerization (Sánchez et al., 2007). Thus, nanocapsules should be obtained from an emulsion copolymerization of methyl methacrylate and glycidyl methacrylate (Alay et al., 2010) or from emulsion polymerization of methyl methacrylate (Sari et al., 2010). Even if, the entrapped PCMs have shown good thermal reliability and chemical stability after 5000 melting and freezing cycling, the PCMs loading content was found relatively poor (Table 1.). Sánchez et al., (2007) have suggested a new microencapsulation method based on a free radical polymerization of styrene to entrap PCMs, where the obtained particles contain almost 50 wt.% of PCMs. Furthermore, to improve the encapsulation efficiency and the storage capacity of the microcapsules, they also suggested to copolymerize styrene with methyl methacrylate (Sánchez et al., 2010).

3.4 New development in microencapsulation process to enhance thermal properties

One of the most limitations of these processes implying polymeric shell is the low heat conductivity and thermal stability of the obtained microcapsules. Although various

methods have been explored for increasing the thermal conductivity of PCMs (Mills et al., 2006), few of them should be transferred to the microencapsulation method. Thus, a literature survey shows that there mainly are two ways to enhance it, either by using metal filler, carbon nanofiller or fiber in the PCMs formulation or synthesize new shell with enhance thermal properties.

On the one hand, Song et al., (2007) have improved the thermal stability of their mPCMs by adding 3 wt.% of silver nanoparticles in the core formulation. Besides, it was observed by Borreguero et al. (2011) that their microcapsules obtained by spray drying and containing Rubitherm®RT27 with 2 wt.% of carbon nanofibers have higher thermal conductivity, which promote a faster heat absorption while maintaining their thermal energy storage capacity.

On the other hand, Salaün et al. (2008c) have observed that the addition of a reasonable fraction of polymeric nanoparticles containing hydrated salt with low thermal conductivity in the PCMs microcapsules results in a decrease by a factor of three of the effective thermal conductivity. They concluded that this outcome was a significant improvement of the thermal barrier in the steady state. In addition, organic-inorganic hybrids have attracted more and more attention in order to combine distinct properties of these two kinds of materials, and specially since the thermal conductivity of inorganic materials is higher than that of organic materials. Thus, Zhang et al. (2010) have chosen a silica shell to synthesize microcapsules with a size distribution between 7 to 16 μm . They observed that the thermal conductivity of their particles increases up to $0.6212 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for a *n*-Octadecane loading content of 52.2 wt.%, which enhanced their heat transfer performance.

4. Textiles containing microencapsulated thermal energy storage compounds

4.1 Historical background

Since 1983 at Triangle Research and Development Corporation (TRDC), Colvin and co-workers have begun investigations to demonstrate the possibility to microencapsulate paraffinic PCM. After having demonstrated the possibility to manufacture textiles containing mPCMs for the Air Force (Bryant & Colvin, 1988), TRDC participated, from 1987, to develop the encapsulation of paraffin for NASA for use in astronaut gloves during extravehicular activities. The patent issued to Triangle R&D in 1988 on the incorporation of mPCMs within a fiber concerned polyester, nylon, acrylics and modacrylics fibers. Then, Bryant & Colvin demonstrated the feasibility of incorporating PCMs, i.e. *n*-eicosane, 2,2-dimethyl-1,3-propanediol and 2-hydroxymethyl-2-methyl-1,3-propanediol, within textiles fibers, patented in 1994 (Bryant & Colvin, 1994). In 1991, Gateway Technologies (Outlast Technologies from 1997) acquired the exclusive patent rights for incorporating phase-change technology in commercial fibers and fabrics from TRDC. Since the 90s, Outlast Technologies have developed and patented several processes to apply microcapsules into textiles structures, to enhance wearer comfort and to provide temperature control for consumers in bedding, medical supplies, sportswear, protective clothing...Furthermore, the microencapsulation of phase change materials and the manufacture of smart textile containing these microcapsules has drawn an increasing interest of researcher from universities in the two past decades, as shown by the amount of published studies on the manufacture and the thermal comfort characterization of these materials (Bendrowska, 2006).

4.2 Performance in clothing

When the mPCMs are applied into textiles substrate, they can absorb heat energy, from the body or from the environment, to go from a solid state to a liquid state, and then create a temporary cooling effect in the clothing layer, until the completed melting of the core material. The reversibility of this effect can be obtained when the smart textile is worn in an environment, where the temperature is below the crystallization point of the PCMs formulation. Thus, the temperature of the smart fabrics falls down below the crystallization point, and when the liquid PCMs change back to a solid state, the heat energy is released to the surrounding medium, which leads to the wearer a temporary warming effect. From these two effects, a thermo-regulating effect should be reached to keep the temperature of the surrounding medium nearly constant. And therefore, this kind of textiles can be reacted as an active thermal barrier effect to regulate the heat flux through the structure and to adapt the heat flux to thermal needs according to the activity level or to the ambient temperature changes (Pause, 2001).

Since the thermal comfort sensation refers to the state of mind that expresses satisfaction with the thermal environment, this feeling is influenced by various parameters, in which the garment design plays an important role. Thus, the use of mPCMs in clothing should act in addition to the passive thermal insulation effect of the garment system. To design specific clothing layer, the mPCMs quantity should be adjusted in regards to the activity level and the duration of the garment worn, bearing in mind to maintain sufficient breathability, flexibility and mechanical stability of the structure. Thus, in order to obtain the desired effect, the manufacturer should pay attention to select the appropriate PCMs formulation, to determine the sufficient quantity of the PCMs, to choose the appropriate fibrous substrate and to design the product (Bendrowska, 2006). On the other hand, the magnitude and duration of thermal effect are dependent upon design textile factors.

4.3 Manufacture of thermoregulated textile structures

The step of encapsulation allows to manufacture textile containing microcapsules by various ways to fix the microcapsules within the fiber structure permanently, to embed them into a binder or to mix them into foam. To produce these textiles, mPCMs should respect these criteria: uniformity of particle size; a core to shell ratio with a PCMs content as high as possible; stability to mechanical action and good thermal and chemical properties.

4.3.1 Lamination

The method to manufacture foam containing mPCMs (between 20 to 60 wt.%) was first described by Colvin & Bryant in 1996. This foam is very useful in the heat-insulating application, since it may be used as a lining for gloves, shoes, or outerwear, when it has been integrated to the textiles complex by glue, fusion or lamination. The advantages of this technology are the use of a greater amount of mPCMs, and also the possibility to incorporate various PCMs formulation to cover a broad range of regulation temperature. Furthermore, the passive insulation should be increased with the formation of honeycomb structure which can entrap considerable amount of air (Sarier & Onder, 2007b). Nevertheless, the interactions between the chemical structure of the microcapsules and the polymeric material used to form the foam may lead to a defoaming process at high loading content as observed by You et al., (2008). Thus, to increase the loading content (up

to 25.2 wt.%) and therefore the enthalpy heat (28 J.g⁻¹), they proposed to synthesize styrene-divinylbenzene (DVB) co-polymer as shell material rather than melamine-formaldehyde (You et al., 2010).

4.3.2 Coating

For a coating process, the wetted mPCMs are dispersed throughout a polymeric binder, a surfactant, a dispersant, an antifoam agent and a thickener, as preconized by Zuckerman et al. (1997). All the common coating processes, such as knife over roll (Pause, 1995), screen printing (Lottenbach & Sutter, 2002; Choi et al., 2004), pad-dry-cure (Shin et al., 2005), knife over air, and gravure and dip coating (Bryant & Colvin, 1996; Zuckerman et al., 2001) should be used. Besides, even if the method for manufacturing coating composition was widely described in the patent literature, nevertheless few papers published in the literature give account of the formulation of coating, finishing of fabrics and therefore the evaluation of their characteristics more specially thermal and durability properties. Furthermore, the use of polymeric binder has some drawbacks, since the incorporated amount should be enough to obtain permanent linkage which can alter the fabric properties such as drape, air permeability, breathability, thermal resistance, softness and tensile strength can be affected adversely as the percentage of binder add-on increases. Salaün et al. (2009a) have proposed a thermodynamical method based on the comparison of the surface energy component to select the most suitable polymeric binder for melamine-formaldehyde microcapsules. They also determined that the polyurethane binder plays a main role during the thirty seconds of a cold to warm transition allowing to delay the temperature increase. Furthermore, the thermoregulating response depends on the surface deposited weight and the mass ratio binder to microcapsules. Thus, an interesting cooling effect is found for 20 g.m⁻² of binder and from 40 g.m⁻² of mPCMs. And a mass ratio binder to mPCMs taken between 1:2 and 1:4 is suitable to manufacture thermoregulating textile (Salaün et al., 2010c). Choi et al. (2004) have coated a polyester fabric by screen printing and knife over role, and they have denoted that the first process allowed to obtain less stiff and hard fabric, and higher air permeability and lower moisture absorption than the other one. Chung et al. (2004) have succeeded in the manufacture of vapour-permeable, water repellent and thermoregulated fabrics, in coating melamine-formaldehyde microcapsules mixed in to polyurethane binder. The amount of heat was kept constant (~14 J.g⁻¹) after 30 launderings, and even if the water repellence property was the same with and without mPCMs, they have also observed a decrease for the water resistance with the presence of mPCMs. On the other hand, Sánchez et al. (2010) have manufactured a cotton coating fabric (with an enthalpy heat about 7.6 J.g⁻¹) with 35% of polystyrene microcapsules related to the coating formulation. They observed a thermoregulatory effect of 8.8, 6.3, 5.6 and 2.5°C after 6, 12, 44 and 75 s. Furthermore, their results after rubbing and ironing tests were higher than those of Kim & Cho (2002).

4.3.3 Spinning

The incorporation of mPCMs within fibers was first patented in 1988 (Bryant & Colvin, 1988). This kind of manufacture presents some advantages as a permanent incorporation and no need to modify subsequent processing and after treatment. Thus, the process to obtain

artificial or synthetic fibers containing mPCMs can be achieved either by wet spinning for e.g. polyacrylonitrile (Lennox, 1998), polyacrylonitrile-vinylidene chloride (Zhang et al., 2005b), acrylic fiber (Cox, 2001), or by melt spinning (Gao et al., 2009) for polypropylene (Leskovšek et al., 2004) or polyethylene fiber (Zhang et al., 2005b). Although, the touch, drape, softness and color were not modified by the spinning process, the thermal heat capacity of the obtained fiber was limited to a low microPCMs loading content. Up to now, the main envisaged way to incorporate microcapsules directly into fibers was solvent spinning rather than melt-spinning because of their tendency to aggregate themselves under dried powder form, and also sometimes because of the high temperatures involved in melt-spinning which could degrade the microcapsules. Thus, since 1997, polyacrylonitrile fibers containing 7 wt.% of microcapsules were put onto market, even if their storage capacity is relatively low (about 8-12 J.g⁻¹). Since, Leskovšek et al. (2004) have shown the possibility of introducing microcapsules into polypropylene fibers in the presence of a lubricant. In their study, the added amount of microcapsules was relatively small (1%, 2% and 5%) and the PP was in the form of a single monofilament yarn with a large diameter. They denoted that the microcapsules did not impair the mechanical properties of the fibres. More recently, in 2005, Zhang and co-workers have succeeded in increasing the loading mPCMs content up to 24% in PP fibers, and they denoted that these fibers exhibited acceptable mechanical properties as the content in mPCMs does not exceed 20 wt.%, for an enthalpy about 11 J.g⁻¹. Wet-spun thermoregulated polyacrylonitrile-vinylidene chloride fibers containing 30 wt.% of mPCMs were also obtained by Zhang et al.(2006). Gao et al. (2009) have shown the possibility to incorporate the mPCMs during the polymerization step of Acrylonitrile-methyl acrylate copolymer before the melt-spinning process. Thus, they obtained thermoregulated fibers containing 20 and 25 wt.% of mPCMs for a melting enthalpy about 21 to 25 J.g⁻¹.

5. Conclusion

One of the advantages of microencapsulated PCMs is their use for the fabrication of any kind of active smart textiles, meaning which sense and react to the conditions or stimulus and thus this technology is attractive to improve clothing comfort and this for a wide and diversified market. MPCMs were firstly developed for use in space suits and glove to protect astronauts from extreme temperature fluctuation during activities in space, specially as a glove liner. Actually, mPCMs are widely used to improve the thermal performance of active wear garment (outwear, sportwear, underwear), shoes lining, accessories, bedding products (comforters, pillows, or mattress covers), and in various activity fields such as building, medical, to enhance the thermo-physical comfort of surgical clothing such as gown, caps and gloves; or as a product which support the effort to keep the patient warm during an operation by providing insulation tailored to the body's temperature; in automotive sector to stabilise the interior temperature or in the seat to reduce unpleasant temperature changes and to keep the skin temperatures more constant. In fact, more than 150 textile companies or brand use mPCMs licensed by Outlast technology.

On the other hand, a new kind of microcapsules, interacting with the absorbed water to promote a cooling effect, has been recently developed to enhance mass transfer. This technology is based on the thermo-chemical heat storage, which present numerous advantages, i.e. high energy density, high discharge power due to high reaction enthalpy,

wide reaction temperature range, high heat and mass transfer rates, fast reaction kinetic, low material prices, non toxic material. Thus, the combination of a porous shell with moisture-sensitive compound as xylitol would be useful for a material design of new functional microparticles for thermal and moisture management (Salaün et al., 2011).

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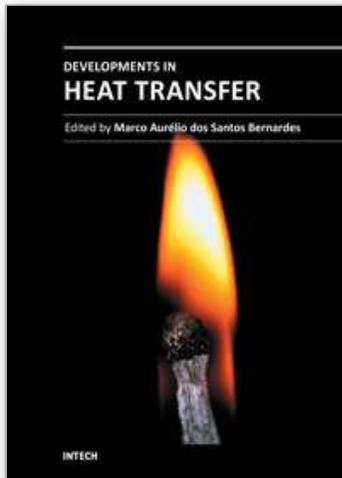
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This book comprises heat transfer fundamental concepts and modes (specifically conduction, convection and radiation), bioheat, entransy theory development, micro heat transfer, high temperature applications, turbulent shear flows, mass transfer, heat pipes, design optimization, medical therapies, fiber-optics, heat transfer in surfactant solutions, landmine detection, heat exchangers, radiant floor, packed bed thermal storage systems, inverse space marching method, heat transfer in short slot ducts, freezing and drying mechanisms, variable property effects in heat transfer, heat transfer in electronics and process industries, fission-track thermochronology, combustion, heat transfer in liquid metal flows, human comfort in underground mining, heat transfer on electrical discharge machining and mixing convection. The experimental and theoretical investigations, assessment and enhancement techniques illustrated here aspire to be useful for many researchers, scientists, engineers and graduate students.

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Phone: +86-21-62489820
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