

Metal salts rented in silica microcapsules as inorganic phase change materials for textile usage

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ABSTRACT

Pure inorganic silica capsules were prepared using polyethoxysiloxane (PAOS) as a cross-linker, and the capsules contain inorganic hydrated salt inside. During this work, six different hydrated inorganic salts evaluated to be used as inorganic phase change materials (namely: calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$), sodium sulphate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and manganese (II) nitrate hexahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)) in silica-based micro-capsules. Inorganic phase change materials have been studied for their application in textiles. The best results are achieved for sodium sulphate decahydrate, and disodium hydrogen phosphate dodecahydrate, respectively. The microcapsules, which show good phase change property, were embedded in a film of the polypropylene at the extruding stage. The basic mechanical properties of the new material do not differ from those of the pure polypropylene.

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KEYWORDS

Inorganic PCM materials;
Textile Fabric;
Microcapsules;
Silica and Polypropylene.

INTRODUCTION

The inorganic phase change materials are largely used for energy storage in various applications including building insulation. They have the important advantage of having high storage density (high enthalpy change at phase transition). On the other side they have the disadvantages of overcooling and corrosion, which impede on their use.

During the present work we evaluated six different hydrated inorganic salts for using as inorganic

phase change materials, namely: calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$), sodium sulphate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and manganese (II) nitrate hexahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). TABLE 1 lists the melting point and enthalpy of fusion for the salts as measured from DSC experiments.

The temperature and heat of fusion given in TABLE 1 indicate that sodium sulphate decahydrate

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TABLE 1 : The melting temperature and the heat of phase transition for several inorganic salt hydrates

| Salt | Formula | Melting temp.(°C) | Enthalpy of fusion (kJ/mole) |
|---|---|-------------------|------------------------------|
| Calcium nitrate tetrahydrate | $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ | 42 | 31.05/132 J/g[7] |
| Calcium chloride hexahydrate | $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ | 29.5 | 43.40/200[7] |
| Sodium sulphate decahydrate | $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ | 32 | 78.20/240-245[8] |
| Disodium hydrogen phosphate dodecahydrate | $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ | 34.5 | 94.9/265[8] |
| Ferric nitrate nonahydrate | $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ | 48.5 | 77.0/190[9] |
| Manganese (II) nitrate hexahydrate | $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 24.8 | 40.26/140[10] |

and disodium hydrogen phosphate dodecahydrate are the most appropriate salts for textile PCM application.

There are various methods for encapsulating the inorganic phase change materials^[1] but the microencapsulation is still a challenge, because of the corrosivity of inorganic salts^(34, 35). For overcoming this we considered the encapsulation in silica based capsules by using poly (ethoxysiloxane) (PAOS, which was synthesized by the polycondensation of tetraethoxysilane as described elsewhere^[2, 3], see structure in Figure 1 to produce capsules with the

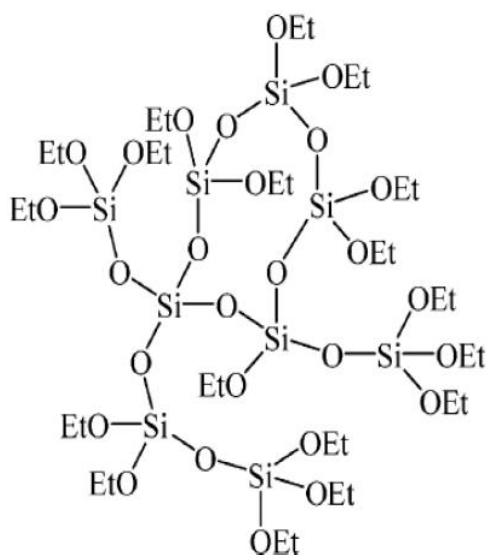


Figure 1 : Molecular structure of poly (ethoxysiloxane) (PAOS)

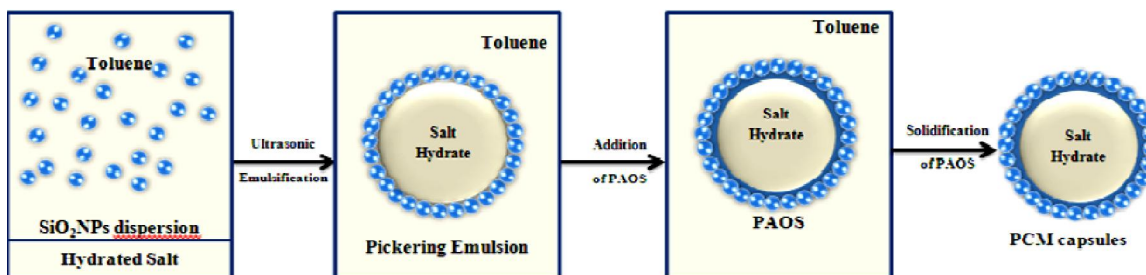


Figure 2: Schematic illustration of the preparation of the inorganic PCM capsules based on silica nanoparticles

core made of hydrated salt.

Silica has several advantages over traditional organic materials. It is an inert, transparent, stable, biocompatible and non-toxic material which makes it the ideal solid matrix for addition of other functionalities.

Though many techniques have been developed for the preparation of capsules with different compositions and structures, the synthesis of inorganic capsules in a controllable manner is still a challenge. We developed a versatile strategy based on Pickering emulsion^[4, 5] to synthesize pure silica nanoparticles with designed structure and properties.

The method for preparation of the silica nanoparticles is outlined in Figure 2.^[6] Water-in-oil emulsion (w/o) was used as a soft template for the synthesis of PCM capsules.

EXPERIMENTAL

Materials

Tetraethyl orthosilicate (TEOS), trimethoxy (octadecyl)silane (MODS), poly (ethoxysiloxane) (PAOS), sodium sulphate decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ disodium hydrogen phosphate dodecahydrate $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, ethanol, toluene, hydrochloric acid and ammonia, all of reagent purity, were acquired from Aldrich Sigma. Polypro-

pylene (PP) grains were received from Sabic.

Methods

Preparation of PCM-silica capsules

Preparation of hydrophobic silica particles

Tetraethyl orthosilicate (TEOS) (208.33 g/mole, 1.67 ml; 7.5×10^{-3} mole) was mixed with 2.5 ml ammonia 25%, dissolved in 50 ml ethanol in closed round flask (100 ml) and stirred at 200 rpm for three day at room temperature. The trimethoxy (octadecyl)silane (MODS) (374.67 g/mole 200 μ l; 4.713×10^{-4} mole) was added drop by drop while stirring at 200 rpm, and the mixture was kept under stirring for another three days at the same speed of 200 rpm. The precipitated particles were separated by removing the solvent with centrifuge at 11000 rpm for 10–20 min. The precipitated particles were w several times with toluene until the ethanol was completely removed. Finally, the particles were re-dispersed in 30 ml toluene to form homogenous dispersion.

Preparation of inorganic PCM capsules

1 ml silica dispersion was dissolved in 8.5 mL toluene in a dry round flask, and mixed with inorganic salts in various ratio of silica to inorganic salt, namely: 5:95, 10:90, 15:85, 20:80 and 25:75 (wt/wt) respectively, and the pH was adjusted at pH = 1 by using 1 ml HCl. The mixture was then emulsified by ultrasonic action for 30 min, after which 0.6 mL from 20% PAOS in toluene was added to the emulsion drop by drop. The emulsion was further kept under gentle stirring at melting temperature of the inorganic salt for at least three days for allowing PAOS to solidify in order to form the capsules. The precipitate was washed with a mixture of ethanol and toluene two – threetimes, followed by once with hexane and twice with toluene, then dried and used for the further analysis.

Preparation film from PCM-silica capsules and polypropylene

The laboratory extruder from DSM Research BV X-Plore was used for manufacturing the films of polypropylene and PCM capsule mixture by extrusion under a flow of nitrogen. The films were pre-

ferred over the fibres, because in case of fibres the change in capsule size could block the nozzles of the spinneret. The capsules were added up to 5% (weight) of the PP grains and the mixture was melted in a twin screw extruder, the temperature being kept at 200°C from top to bottom. The mixing speed was 100 rpm and the screw speed was 35 U/min, the drawing speed at 850 mm/min and the torque was 30 rpm. The extruded film was 90–100 μ m thick.

Coating of wool and cotton fibres/fabrics with PCM compound

A coating method was applied to prepared PCM materials with 100% cotton and wool fibres. Coating material is a water soluble synthetic dispersion, commercially available for fabrics, that was polyurethane based, anionic, with 45–48% active content. Fixing agent comprising melamine resins with low formaldehyde content, which was miscible in water, nonionic and of 8–9 pH value was used for cross linking.

Recipes were prepared for 1:1 and 1:1.5 mixtures of the coating material and the PCM materials. Ten units coating material were stirred at 600 rpm for 5 min and then 10 or 15 units PCM material were mixed while increasing the stirring rate up to 1000 rpm for the next 15 min. 1.5% fixing agent was blended and stirring rate was halved for the last 2–3 min.

The fabrics were immersed into the coating dispersion solution at 40–50°C, coated fabric samples were fixed in a drying oven for 15 min and the temperature increased gradually from 60 to 80°C and then conditioned for the subsequent 24 h.

To determine the actual incorporation percentages of the PCM materials transferred to the sample, which depends also on the coating thickness, we weighed the coated and uncoated pieces of fabric.

MEASUREMENTS

Differential scanning calorimetry (DSC)

DSC measurements for measuring the melting and the crystallization behaviour of the substances were carried out on Perkin Elmer DSC and on Netzsch DSC 204. The measurements were run using nitro-

Full Paper

gen flow at 20 ml/min as purge gas. The weighted samples, each of approximately 7 mg, were closed in aluminium pans, which were perforated prior to be placed in DSC device. An empty aluminium pan was used as reference. The temperature programme consisted of heating, cooling and heating steps. Temperature ranged from 0°C to 70°C, with 10 K.min⁻¹. The melting temperature and enthalpy ΔH were evaluated from the onset and area, respectively, of the peaks recorded during the second heating. DSC temperature and heat flow was calibrated with indium.

Scanning electron microscopy (SEM)

Scanning electron microscope (SEM) measurement of the PCM capsules was carried out on Hitachi 5-4800 FESEM (Field-Emission SEM). The electron beam accelerating voltage was set at 120 kV. The capsules were dispersed in toluene, and one drop of the dispersion was trickled on a piece of form var-carbon coated copper grid. Before placed into the SEM, the copper grid was dried in air under ambient conditions.

Surface morphology and the cross section of the composite films were studied using scanning electron microscope HITACHI S-3000 microscope S, at 15 kV acceleration voltage, after gold coating.

Mechanical properties

The film of PP/PCM was measured for mechanical properties on a Miniature Materials Tester (MiniMat2000 by Rheometric Scientific). Prior to measurement the sample was kept for 24 hours at 22°C and relative humidity of 65%. After mounting the sample in the tester it is stretched with a constant rate of 0.1 mm/min under a load of 20 N until the break.

RESULT AND DISCUSSION

Encapsulation into silica particles

The weight ratio of hydrophobic silica particles to PCM salt ranged from 5:95 to 10:90, for preserving as much as possible of heat storage ability. The ratio is further decreased in the final product because the amount of PAOS which forms the shell is

not well controllable. The obtained capsules properties are 60 – 125 nm capsules radius with 10 – 30 nm wallthickness for Na₂SO₄.10H₂O/Silica and 45 – 80 nm capsules radius with 10 – 20 nm wallthickness for HNa₂PO₄.12H₂O/Silica, and the capsules were measured on DSC see Figure 3, and the DSC values are listed in TABLE 2.

Scanning electron microscope micrograph show that the particle size is within the micrometer range (2-3 μ can be detected) see Figure 4. Results in TABLE 2 indicate that the encapsulation preserves the effect of PCM, but the size of the effect is reduced according to the overall percentage of salt to silica capsule. It appears also that the heat transmission coefficient of the silica shell shifts the phase transition peak to higher value, and also rounds the endothermic peak shape.

Textile application

The DSC results of coated cotton and wool fabrics with inorganic PCM polymer composites (Na₂SO₄.10H₂O + Silica and HNa₂PO₄.12H₂O + Silica) are listed in TABLE 3. One may conclude

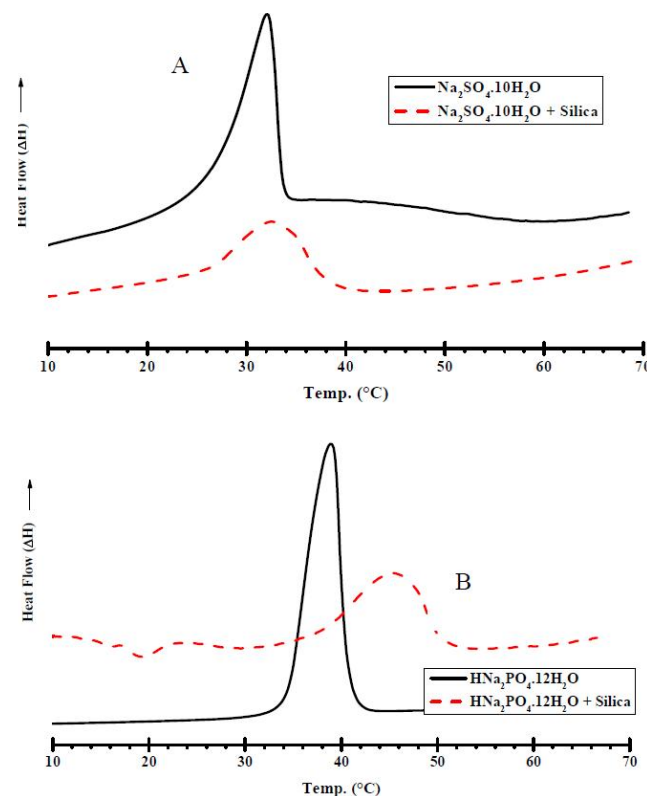


Figure 3: The DSC plots of silica capsules containing Na₂SO₄.10H₂O (A) and HNa₂PO₄.12H₂O (B)

TABLE 2 : DSC data for PCM materials from hydrated inorganic salts with silica particles

| Material | 1 st Heating | | 2 nd Heating | |
|---|-------------------------|----------|-------------------------|----------|
| | T _o (°C) | ΔH (J/g) | T _o (°C) | ΔH (J/g) |
| Na ₂ SO ₄ .10H ₂ O | 27.9 | 234.6 | 27.2 | 230.2 |
| Na ₂ SO ₄ .10H ₂ O + Silica | 27.3 | 38.6 | 29.0 | 35.4 |
| HNa ₂ PO ₄ .12H ₂ O | 37.4 | 266.7 | 37.4 | 250.0 |
| HNa ₂ PO ₄ .12H ₂ O + Silica | 36.6 | 69.3 | 36.3 | 70.1 |

T_o: Onset Temp (°C) ΔH: Enthalpy, (J/g)

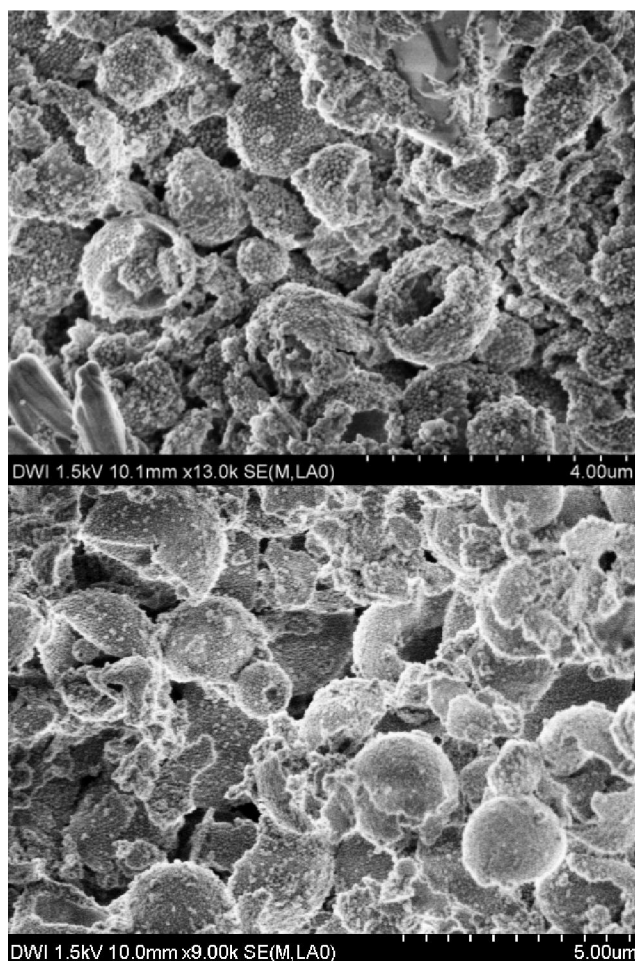


Figure 4 : Inorganic PCM encapsulated in silica particles

that wool and cotton fabrics can be coated with inorganic PCM polymer composite. The abrasion/washing tests indicate a fairly good stability of the thermal buffer effect imparted by coating.

Polypropylene film with PCM-silica capsules

Polypropylene (PP) is a highly versatile polymer used mainly for interior textiles. We chose this material to embed PCM silica capsules, for increasing its heat storing capacity. The PP grains were mixed with 5% PCM-silica capsules and the film was extruded at 200°C as described previously.

The elongation at break of 6% was recorded for films with 5% PCM capsules. This is within the range recorded for pure PP film (5 – 6%), indicating that the capsules do not affect the mechanic properties of the polypropylene film.

The DSC plots of the PP film embedding 5% PCM capsules with sodium sulphate decahydrate, or disodium hydrogen phosphate dodecahydrate, respectively, are shown in Figure 5, along with the plot of a PP film, for temperature ranging from room temperature to 80°C with 10°C/min.

One observes the endothermic peak of PCM capsules with sodium sulphate decahydrate around 53°C due to the phase transition (melting) of sodium sulphate decahydrate. The size of the effect is very

TABLE 3 : DSC and DI results of coated fabric with inorganic PCM polymer composites

| Polymer | Fabric Type | 2 nd Heating | | | |
|---|-------------|-------------------------|----------|---------------------|----------|
| | | After treatment | | After washing | |
| | | T _o (°C) | ΔH (J/g) | T _o (°C) | ΔH (J/g) |
| Na ₂ SO ₄ .10H ₂ O + Silica | Cotton | 28.8 | 34.1 | 29.2 | 32.2 |
| | Wool | 28.9 | 36.8 | 28.8 | 35.8 |
| HNa ₂ PO ₄ .12H ₂ O + Silica | Cotton | 36.5 | 68.2 | 36.9 | 67.4 |
| | Wool | 36.7 | 72.5 | 37.2 | 71.3 |

T_o: Onset Temperature °C,

ΔH: Enthalpy J/g

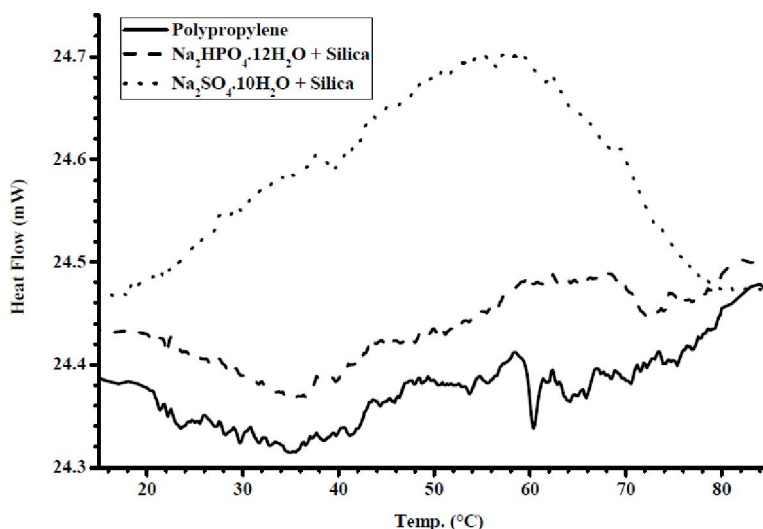


Figure 5 : DSC plots of films of PP and PP with PCM capsules from $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{HNa}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$

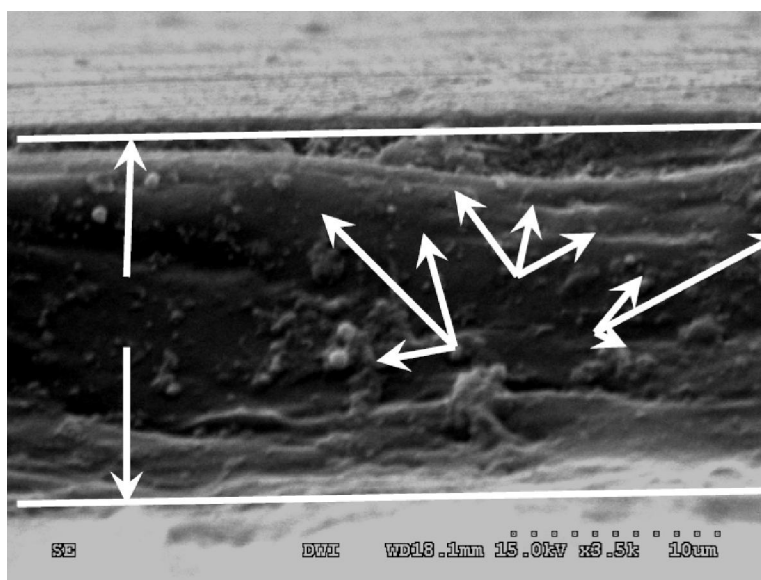


Figure 6: Cross-section of poly propylene film with 5% PCM capsules

small, at about 2 J/g materials, and can be increased by increasing the amount of PCM capsules added to PP film.

Figure 6 shows the SEM micrographs of the PCM-silica capsules distributed in the cross-section of a polypropylene film extruded from polypropylene melt with 5% added capsules. The micrographs indicate a homogeneous distribution of the capsules in the PP film, showing a good compatibility of the additive and polymer matrix.

For the textile use the methodology set up for films can be transferred for fibres. The fibres with encapsulated PCM materials are the most advantageous technique to merge the expected enriched heat

performance with the other textile properties on the same product. Also it is a good way to avoid the interaction of the PCM materials with the skin. The incorporation of PCM capsules into textiles in the form of a core-shell matrix brings many opportunities such as less evaporation and minimum interaction with the environment, increased heat transfer area and long shelf-life of the garment.

CONCLUSIONS

The possibility to encapsulate inorganic PCM in an inorganic silica-based capsule, and used the capsules for coating or infiltrating them on/into films/

fibre have been investigated.

Capsules contain inorganic hydrated salt inside. We successfully produced silica-based microcapsules with sodium sulphate decahydrate, and disodium hydrogen phosphate dodecahydrate respectively. The microcapsules, which show retaining good phase change property, were embedded in a film of the polypropylene at the extruding stage. The basic mechanical properties of the new material do not differ from those of the pure polypropylene. The DSC data indicate that the effect of the phase change material (melting of the salt), is measurable also in the film. The capsules were also used for coating textiles of wool, or cotton. The DSC data indicates that the effect is preserved after washing of the textile.

Summing up, we have produced polymer-inorganic PCM materials which show potential for being used in textile industry for interior textile composition.

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