

New polyurethane/docosane microcapsules as phase change materials for thermal energy storage

P.F. De Castro^{*[a]} and D.G. Shchukin^[b]

Abstract: Polyurethane microcapsules were prepared by mini emulsion interfacial polymerization for encapsulation of phase-change material (n-docosane) for energy storage. Three steps were followed with the aim to optimize synthesis conditions of the microcapsules. First, polyurethane microcapsules based on silicone oil core as an inert template with different silicone oil/poly(ethylene glycol)/4,4'-diphenylmethane diisocyanate wt % ratio were synthesized. The surface morphology of the capsules was analyzed by scanning electronic microscopy, SEM, and the chemical nature of the shell was monitored by Fourier transform infrared spectroscopy, FT-IR. Capsules with the silicone oil/poly(ethylene glycol)/4,4'-diphenylmethane diisocyanate 10/20/20 wt % ratio showed the best morphological features and shell stability with average particle size about 4 μm and were selected for the microencapsulation of the n-docosane. In the second stage, half of the composition of silicone oil was replaced for n-docosane and, finally, the whole silicone oil content was replaced with docosane following the same synthetic procedure as for silicone oil containing capsules. Thermal and cycling stability of the capsules was investigated by thermal gravimetric analysis, TGA, and the phase change behavior was evaluated by differential scanning calorimetry, DSC.

Introduction

Microencapsulation has been widely applied in a variety of fields such as drug delivery, cosmetics, textiles, adhesives, insecticides, corrosion, inhibitors, lubricants and so on^{1,2,3,4}. Microcapsules are small particles that contain an active agent or core material surrounded by a coating or shell to protect the core cargo and to release it into an outer phase in a controlled way.

There are several types of thermal energy storage systems: sensible heat, latent heat and chemical systems. Sensible and latent heat have been studied as of major importance. The advantage of the sensible heat storage is its simplicity but the major drawback is its poor energy storage density due to large

volume of the system required to store small amount of energy. Using phase change materials (PCMs), the energy storage density of the system is increased due to the latent heat involved. PCMs have been studied since they can absorb or release the thermal energy equivalent to their latent heat when they undergo or overpass the phase transition in a quasi-isothermal process. Among the disadvantages of PCMs are the low heat transfer, poor stability during energy uptake/release and their difficulty to be handled in practical applications⁵. In this regard, microencapsulation can be the option to increase the heat transfer area of the PCM systems containing the liquid phase during the solid-liquid phase change⁶, to stabilize them against environmental degradation and to improve their handling and installation. The microencapsulated PCMs can find applications in thermal regulating textiles⁷, and as materials in solar energy storage systems⁸.

Among all the microencapsulation techniques mini-emulsion interfacial polycondensation is one of the most convenient and feasible in the preparation of micro or nanocapsules⁹. It consists of an emulsion of two immiscible phases (i.e., oil and water, O/W) where each phase contains a dissolved monomer that is able to react with the other monomer presented in the other phase. The microencapsulation takes place at the interface of the droplets between the two monomers entrapping in situ the oil or water core.

In this research polyurethane (PU) was selected as a capsule shell material because of a) great spectra of chemical and mechanical properties that can be obtained by varying the chemical nature and molecular weight of the soft (polyols) and hard components (diisocyanates and chain extenders)^{10,11}, b) high elastic properties, strength and smooth surface^{12,13} and c) the advantage of non-formaldehyde content in comparison with other shells with similar properties such as melamine-formaldehyde (MF) resin and urea-formaldehyde (UF) which have widely been used for the microencapsulation of phase change materials but generate environmental and health problems related with the release of formaldehyde^{14,15}. As a core material, n-docosane was chosen as a PCM because of its large latent heat of fusion (248 J/g) and melting point of about 41 $^{\circ}\text{C}$ ¹⁶. It, therefore, may be used in various products such as thermal regulated fibers, fabrics, foam, solar heating materials¹⁷, where medium temperatures are required. In the beginning, the encapsulation methodology was developed using silicone oil as an inert template with high solubility to docosane. The optimized synthesis conditions were used on the following stages to encapsulate 50 % and 100 % of the n-docosane. As far as the authors are aware, there is no research reported in literature on preparation of PU/n-docosane as microencapsulated PCMs.

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Results and Discussion

SEM micrographs of the microcapsules with the silicone oil used as a template are shown in Figure 1. These images indicated that spherical microcapsules were obtained for all the compositions with some of the microcapsules folded inwards due to the vacuum treatment done during SEM sample preparation.

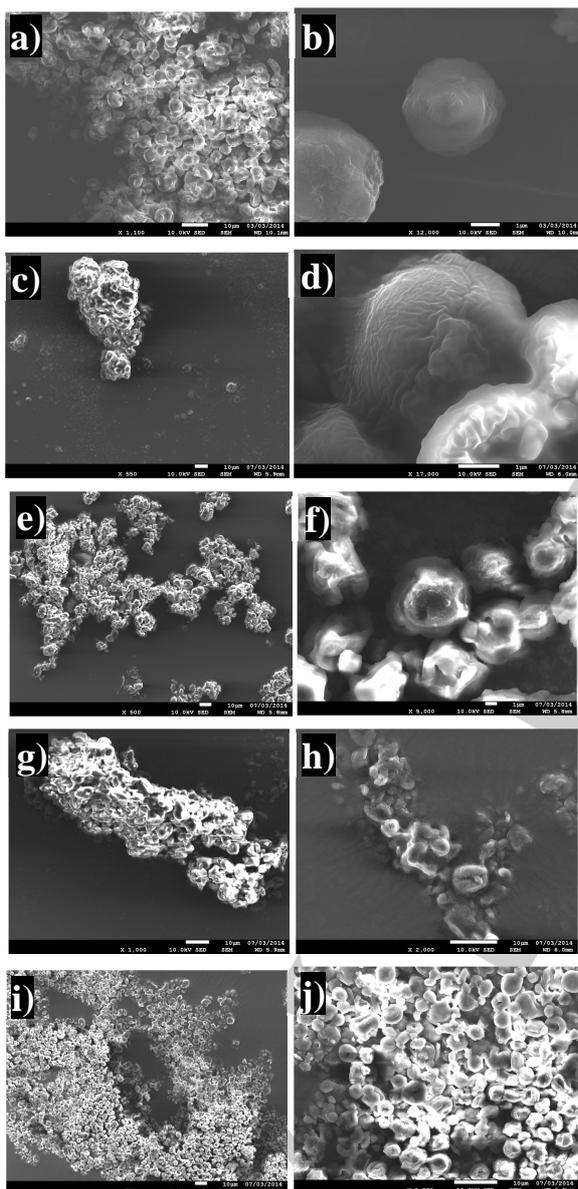


Figure 1. SEM images of the silicone-loaded PU capsules. Sample compositions (silicone oil/PEG1000/MDI): a), b) 10/20/20; c), d) 10/10/10; e), f) 10/5/5; g), h) 15/15/15 and i), j) 10/15/15.

Capsules with silicone oil/PEG1000/MDI composition 10/20/20 and 10/15/15 show no aggregates while samples with compositions 10/10/10, 10/5/5 and 15/15/15 show interconnectivity between the capsules and cluster formation. Higher magnification of these samples revealed that the microcapsules have a wrinkled surface morphology unlike the surface morphology of the first two samples with compositions 10/20/20 and 10/15/15. It was also found that the average microcapsule size is $\sim 4 \mu\text{m}$ for the capsules with composition 10/20/20 and $\sim 5 \mu\text{m}$ for the ones with composition the 10/15/15. The particle size of the other samples was not measured due to the aggregated state. The composition 10/20/20 was chosen for the microencapsulation of n-docosane due to the smallest size and spherical, non-aggregated appearance.

The FT-IR spectra of the capsules with silicone oil are shown in Figure 2. The characteristic peaks of the silicone oil are observed in the spectrum of the oil microencapsulated by PU shell: asymmetric and symmetric stretching vibration of the $-\text{CH}$ of the methylene group at 2961 and 2904 cm^{-1} , stretching vibration of the $-\text{C}=\text{C}$ of the aromatic ring at 1595 cm^{-1} , asymmetric and symmetric deformation of the $-\text{CH}_3$ of the $-\text{Si}-\text{CH}_3$ at 1412 and 1257 cm^{-1} , stretching vibration of the $-\text{Si}-\text{O}-\text{Si}$ at 1009 cm^{-1} and the stretching vibration of $-\text{Si}-\text{C}$ at 787 cm^{-1} . The characteristic peaks of the PU shell are also observed: the hydrogen-bonded and non-bonded NH stretching vibration at 3300 and 3360 cm^{-1} , respectively, stretching vibration of the free and associated CO of the urethane group at 1730 and 1700 cm^{-1} , respectively, absorption of urea group at 1637 cm^{-1} , stretching vibration of the $-\text{C}=\text{C}$ of the aromatic ring of the diisocyanate at 1594 cm^{-1} , stretching vibration of the CN group and deformation of the NH_{assoc} at 1539 cm^{-1} , deformation of the NH_{assoc} and stretching vibration of the CN at 1300 cm^{-1} , deformation of the CN and stretching vibration of the CO_{assoc} at 1230 cm^{-1} and the stretching vibration of the $(\text{C}-\text{O}-\text{C})$ at 1095 cm^{-1} . The appearance of characteristic peaks of silicone oil and PU in the microencapsulated silicone oil indicates the PU shell has formed and, as a consequence, the silicone oil has been successfully encapsulated. The spectrum also contains the absorption peak of the $-\text{NCO}$ group at 2270 cm^{-1} which means there is still unreacted diisocyanate, probably inside PU shell.

Figure 2. FT-IR spectra of a) silicone oil, b) PEG1000, c) MDI and d) silicone oil microencapsulated into polyurethane shell.

On the next stage, 50% of the silicone oil was replaced for docosane. SEM images of the microcapsules based on silicone oil and n-docosane with 50% silicone oil + 50% n-docosane/PEG1000/MDI composition 10/20/20 wt % are shown in Figure 3. The replacement of the half of the silicone oil for n-docosane was successfully achieved. Capsules with spherical shape were obtained with rougher surface comparing to the microencapsulated pure silicone oil.

PU capsules with silicone oil and n-docosane have non-porous and smooth surface while previously reported docosane-loaded melamine formaldehyde capsules are porous and do not protect the spontaneous interaction between encapsulated docosane and environment^{17,18}.

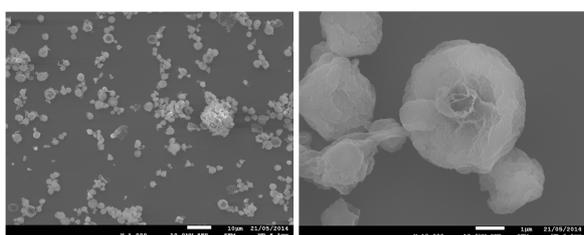


Figure 3. SEM images of the sample compositions (50% silicone oil + 50% docosane)/PEG1000/MDI with 10/20/20 wt % ratio.

On the last step, we completely replaced silicone oil for the n-docosane. The n-docosane/PEG1000/MDI wt % ratio was 10/20/20 following the same synthesis procedure of mini-emulsion interfacial polymerization as described before for pure silicone oil. Different washing treatments were carried out in order to study the washing effect on the capsule separation and stability. Capsules were washed with 30 % ethanol solution, distilled water and with both 30 % ethanol mixture and distilled water. The SEM images of the differently washed capsules are shown in Figure 4. As seen from the images, capsules obtained without any washing have spherical shape and smooth, non-porous surface (Figure 4a and 4b). Some of these capsules are interconnected by large amount of polymer surrounding them which was remained in initial solution after polymerization reaction.

The images of the microcapsules washed with 30 % ethanol in water (Figure 4c and 4d) show aggregates and some of these capsules, at higher magnification, (Figure 4d) are not spherical with rougher surface than for the microcapsules without any washing. One can conclude that resulting PU capsules are not well stable. Similar results were observed for consecutive washing with 30 % ethanol and pure water (Figure 4e and 4f). On the contrary, washing of docosane-loaded capsules with distilled water only (Figure 4g and 4h) leads to the non-aggregated capsules with spherical shape and partly folded surface and without unreacted polymer outside the capsules.

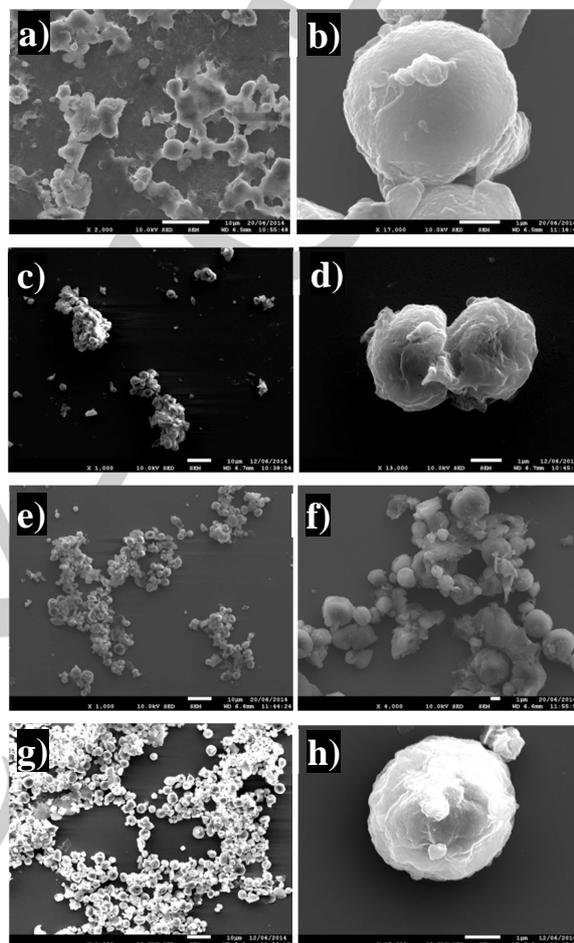


Figure 4. SEM images of microencapsulated n-docosane in polyurethane shell a), b) without washing treatment; c), d) 30 % ethanol washing, e), f) 30 % ethanol plus distilled water washing and g), h) distilled water washing.

FT-IR spectra of the synthesized microcapsules, the pure core material and shell components are presented in Figure 5. The characteristic peaks of the n-docosane: stretching vibration of the $-(CH_2)$ group of the aliphatic chain at 2952, 2913 and 2847 cm^{-1} , stretching vibration of the $-(C-H)$ group at 1369 cm^{-1} and the rocking vibration of the $-(CH_2)$ group at 716 cm^{-1} appear in the microencapsulated n-docosane by PU shell. Characteristic peaks of the PU shell are also observed: the hydrogen-bonded and non-bonded NH stretching vibration at 3300 and 3360 cm^{-1} respectively, stretching vibration of the free and associated CO of the urethane group at 1730 and 1700 cm^{-1} , respectively, absorption of urea group at 1637 cm^{-1} , stretching vibration of the $-(C=C)$ of the aromatic ring of the diisocyanate at 1594 cm^{-1} , stretching vibration of the CN group and deformation of the NH_{assoc} at 1539 cm^{-1} , deformation of the NH_{assoc} and stretching vibration of the CN at 1300 cm^{-1} , deformation of the CN and

stretching vibration of the CO_{assoc} at 1230 cm^{-1} and the stretching vibration of the (C–O–C) at 1095 cm^{-1} .

So, FT-IR spectrum of the microencapsulated n-docosane by PU shell shows a series of strong absorption bands which correspond to both the PCM core and shell components of the microcapsules. There is no evidence of hydroxyl groups (–OH) in the region of 3300 cm^{-1} from the emulsifier¹⁹ which means it does not remain in the obtained microcapsules.

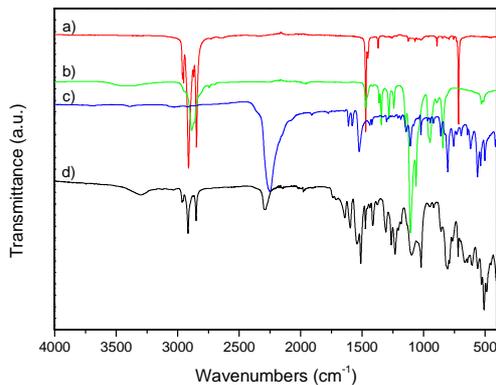


Figure 5. FT-IR spectra of a) n-docosane, b) PEG1000, c) MDI and d) microencapsulated n-docosane in polyurethane capsules.

The microencapsulated n-docosane by the PU shell decomposes at high temperature in two clearly exothermic steps, as shown from TGA analysis in Figure 6. The first decomposition starts at 228 °C with a maximum of weight loss rate at 259 °C and finishes at 264 °C with a 47 % of total weight loss. The second one starts at 449 °C with a maximum of weight loss rate at 522 °C and the decomposition finishes at 571 °C corresponding to 97 % of total weight loss. Low amounts of residue are observed at 600 °C (3%). Thermal analysis of hollow microcapsules based only on PUshell (PEG1000 and MDI) shows two steps of decomposition as it was seen in the microencapsulated n-docosane. First step of decomposition takes place at 238 °C with a maximum of weight loss rate at 244 °C and finishes at 249 °C with a 19 % of weight loss. The second decomposition starts at 462 °C with a maximum of weight loss rate at 510 °C and the decomposition ends at 531 °C corresponding to 89 % of total weight loss and with an amount of residue of 11 % at 600 °C .

Higher weight of loss of PUshell/docosane at $238 - 260\text{ °C}$ (47 %) than for the pure PUshell is attributed to the simultaneous decomposition of docosane at PU decomposition temperature range.

According to the previous studies^{20,21} on thermal decomposition and degradation of PU, the first step corresponds to the breakage of the polyurethane shell, decomposition of the soft segment (PEG1000) of the PU shell and the decomposition of the n-docosane as a consequence of its releasing. The second step corresponds to the decomposition of the hard segment (MDI) of the both PU and PUshell/docosane^{22,23}.

The microencapsulated n-docosane by polyurethane shell obtained in this research presented higher temperature of decomposition around 228 °C than the previously microencapsulated n-docosane by poly(methyl methacrylate) obtained by Fu et al.¹⁸ which decomposed at 150 °C .

Thermal cycling stability of the microencapsulated n-docosane at application temperature range ($25\text{ °C} - 80\text{ °C}$) is shown in Figure 7. The microcapsules show no significant change in their heat flow properties after repeated cycles of heating and cooling.

The microcapsules loaded with n-docosane presented a starting melting temperature of $T_{\text{onset,m}} = 37\text{ °C}$ and melting temperature of $T_m = 42\text{ °C}$ on the heating scan. On the cooling, starting crystallization temperature of $T_{\text{onset,c}} = 38\text{ °C}$ and crystallization temperature of $T_c = 34\text{ °C}$. On the contrary, the $T_{\text{onset,m}}$ and T_m for bulk docosane are 42 °C and 45 °C , respectively, and $T_{\text{onset,c}}$ and T_c are 43 °C and 40 °C , respectively. The difference in temperature between encapsulated and bulk docosane ($\sim 5\text{ °C}$) indicates the effect of the spatial confinement on the thermal characteristics of phase change materials.

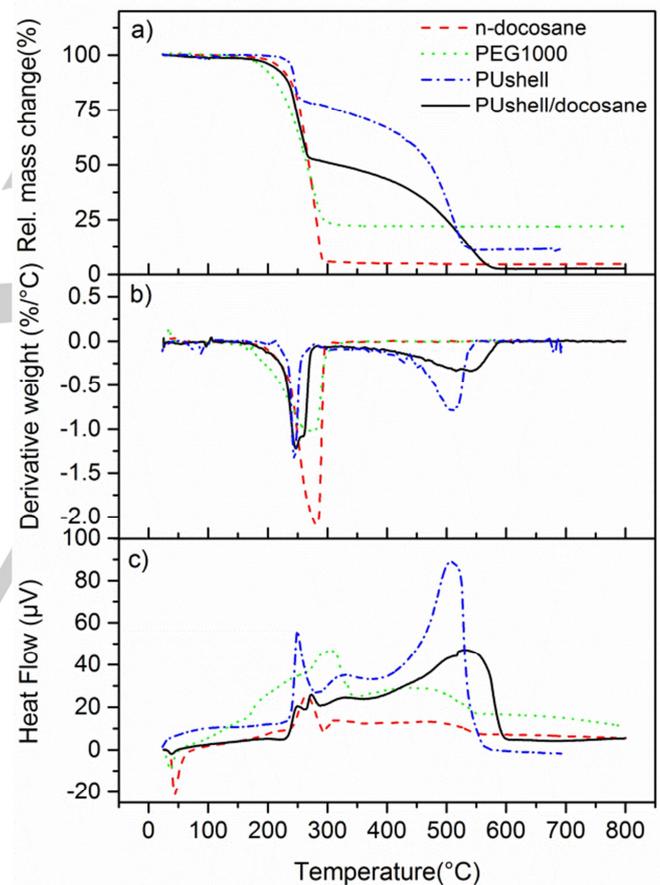


Figure 6. a) Thermogravimetric analysis (TGA), b) Derivative weight (%/°C) and c) Heat flow (μV) of the pure n-docosane, PEG1000 (shell component), PUshell (PEG1000+MDI) and docosane-loaded polyurethane capsules.

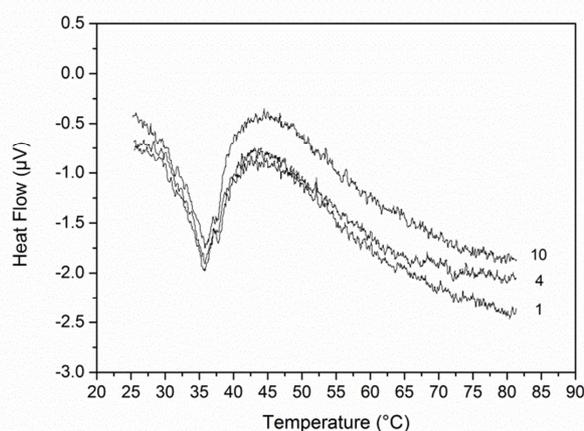


Figure 7. Heat flow of the microencapsulated n-docosane in polyurethane shell during 10 cycles of heating and cooling; 1st, 4th and 10th cycle are shown.

Conclusions

Polyurethane capsules with pure silicone oil as an inert template, 50%docosane/50%silicone oil and 100 % docosane as a cargo material were successfully synthesized by mini-emulsion interfacial polymerization at docosane/poly(ethylene glycol)/4,4'-diphenylmethane diisocyanate 10/20/20 wt% ratio. Resulting capsules are intact, non-aggregated and have average diameter of 4 μm , not depending on the core composition as shown by FT-IR and SEM.

The capsules demonstrated high stability during heat upload/release cycles, as was seen by thermal analysis. Encapsulation of docosane lead to the shifting of the phase transition temperature from 42 $^{\circ}\text{C}$ for the bulk doco sane to 37 $^{\circ}\text{C}$ for the encapsulated one demonstrating spacial confinement effect of the polyurethane shell.

Experimental Section

Materials and methods

Poly(ethylene glycol) (PEG1000, $M_w = 1000$ g/mol), 4,4'-diphenylmethane diisocyanate (MDI) were used for capsule fabrication. Silicone oil was used as an inert template and n-docosane used as a definitive core to obtain the PCM-loaded energy capsules.

Poly(vinyl alcohol) (PVA, 89 % hydrolysed) and dibutyl tin dilaurate (DBTDL) were selected as a surfactant and catalyst, respectively, which promote the reaction between isocyanate and alcohol producing polyurethane and terminate polyurea formation from isocyanate and water. The first reaction was preferred with the aim to obtain microcapsules with low shell porosity and permeability²⁴. Toluene was used as the organic phase and distilled water was used as the aqueous phase. All chemicals were purchased from Sigma Aldrich at a reagent grade and used without further purification.

Synthesis of the capsules

First, encapsulation methodology was developed using silicone oil as a core template. Several compositions of microencapsulated silicone oil with polyurethane shell were prepared at different silicone oil/PEG1000/MDI wt % ratio: 10/20/20, 10/10/10, 10/5/5, 15/15/15, 10/15/15. The composition 10/20/20 was the best composition which gave the excellent surface morphology and desired size of the capsules. This composition was used on the second stage to replace 50 % of silicone oil for n-docosane. Finally, in the last stage, silicone oil was completely replaced for n-docosane obtaining microcapsules loaded with n-docosane only. Different washing procedures were applied to the prepared capsules in order to see the effect of washing on the capsule morphology. The synthesis of the microcapsules by mini-emulsion interfacial polymerization is illustrated in Figure 8.

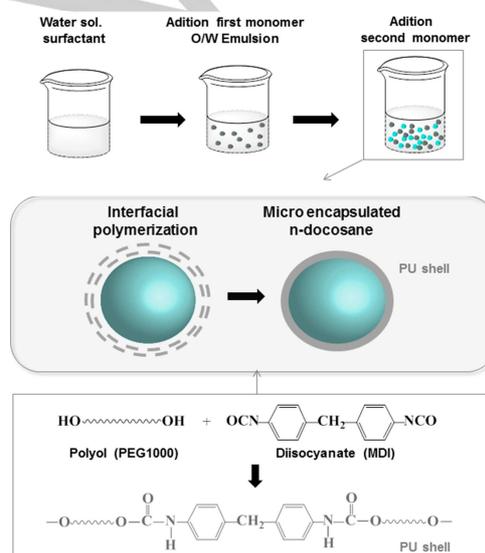


Figure 8. Synthesis of microencapsulated n-docosane with polyurethane shell by mini-emulsion interfacial polymerization.

The O/W emulsion was formed by adding an organic solution containing MDI, n-docosane and toluene to an aqueous solution of 2 wt. % PVA as a stabilizer and stirring the emulsion at 800 rpm. Subsequently, the resultant emulsion was emulsified for 1 min with a homogenizer at 12000-15000 rpm. A milky emulsion was obtained and then heated up to 60 $^{\circ}\text{C}$. When the temperature reached 60 $^{\circ}\text{C}$, a solution containing PEG1000 and a catalytic content of DBTDL as a catalyst was slowly poured into the emulsion and left for 2 hour at 70 $^{\circ}\text{C}$. The reaction between PEG1000 and MDI produces a polymer wall on the emulsion globules. The resultant microcapsule slurry was decanted and filtered. The capsules were washed three times with mixture of ethanol and water and pure water to remove the unreacted isocyanate and silicone oil. After the washing they were dried in the oven at 50 $^{\circ}\text{C}$ for 20 h.

Characterization

FT-IR Spectroscopy. The reagents and prepared capsules were analysed on a Thermo Scientific Nicolet iS50 FT-IR spectrophotometer provided with diamond crystal/ built in all-reflective diamond ATR. All spectra were obtained in absorbance mode and then converted to transmittance mode.

Scanning electron microscopy (SEM). The morphology of the capsules was examined using a JSM-7001F Scanning Electron Microscope from JEOL. The microcapsules were dispersed in distilled water and then a drop was dipped onto a double-side carbon tape on an aluminium SEM stub and dried overnight at room temperature. The samples were coated with chromium and examined.

Thermal Gravimetric Analysis. This technique was used to investigate the thermal and cycling stability of the prepared capsules using a microbalance model STA PT1000 from Linseis. For the thermal stability measurements the samples were heated at 5 °C/min from 25 °C to 700 °C in a stream of air. Thermal cycling test was conducted to determine the thermal reliability of the microcapsules. The test was done consecutively up to 10 cycles of heating and cooling in the range temperature of the docosane phase change from 20 °C to 80 °C at 1 °C/min in a stream of air.

Differential Scanning Calorimetry. The phase change behaviour was evaluated using a calorimeter model Q20 from TA Instruments. Samples were heated and cooled at 10 °C/min from -40 °C to 160 °C in a nitrogen atmosphere. Phase change temperatures such as the starting melting and melting temperatures on heating, $T_{\text{onset,m}}$ and T_m , and starting crystallization and crystallization temperatures on cooling, $T_{\text{onset,c}}$ and T_c , respectively, were obtained.

Acknowledgements

The authors are thankful the EU FP7 BYEFOULING project for financial support.

Keywords: Encapsulation • PCM • n-docosane • energy capsules •

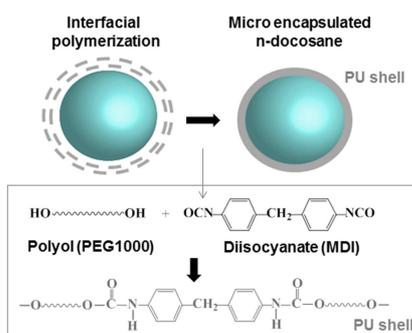
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Entry for the Table of Contents

Layout 1:

FULL PAPER

Energy capsules synthesised by encapsulation of phase change material, n-docosane, into elastic polyurethane shell.

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New polyurethane/docosane microcapsules as phase change materials for thermal energy storage