Highly Stable Hexamethylolmelamine Microcapsules Containing *n*-Octadecane Prepared by *In Situ* Encapsulation

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ABSTRACT: A systematic study has been carried out to investigate the effect of formaldehyde-to-melamine molar ratio varying from 2.5 to 8, core-to-wall ratio from 1 to 4 and curing conditions used during the encapsulation process on the properties of microcapsules that contain *n*-octadecane as the core material and melamine-formaldehyde as the wall material. The microcapsules so obtained were characterized for their core content, encapsulation efficiency, thermal, and solvent stabilities. Using the modified encapsulation process with a formaldehyde- to-melamine ratio of 8 and core-to-wall ratio of 2, microcapsules with a high core content of (70%) and a heat storage capacity of >160 J/g could be obtained. The capsules were found to be stable upto a temperature of 100°C and also stable to cyclohexane wash. A thermoregulated fabric was also prepared by coating the capsules on a cellulose-polyester fabric to give a heat storage capacity of >100 J/g. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2997–3002, 2009

Key words: phase change material; melamine resin; microcapsules; *in situ* polymerization; thermoregulated fabric

INTRODUCTION

Encapsulation is a process of entrapping a tiny core material, typically a small solid particle, or a liquid droplet, or a gas bubble inside a wall material. The core material can be drugs, proteins, antimicrobial agents, hormones, dyes, fragrances, flame retardants, and phase change materials. The wall material is a natural or synthetic polymer. The potential applications of microencapsulation in textile finishing include insect repellent, aroma, antimicrobial agents, antibiotic, polychromic, thermochromic, and flame retardant finishes. Recently, development of thermoregulated textiles using encapsulated phase change materials (PCMs) has gained tremendous interest worldwide.[1]

Useful PCMs for the textile applications are those that change the phase of the materials from solid to liquid by absorbing large amount of latent heat from the environment and from liquid to solid by releasing the same amount of heat to the environment at a transition temperature close to the body temperature.[2]

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Suitable PCMs that satisfy the major requirements of thermoregulation for application in textile clothing are *n*-octadecane, *n*-eicosane, and lithium nitrate trihydrate. The material *n*-octadecane is particularly important because its melting temperature is very close to the comfort temperature of the body, i.e., around 28–29 °C, and it has a high latent heat of fusion of 240 J/g.[3,4] However, this PCM requires to be encapsulated using a suitable technique that can provide high wall integrity and stability. This requirement of better wall integrity is unlike other microencapsulation processes used in finishes, where micropores in the wall membrane are necessary for slow release of drug, perfumes, etc. that are present as core.

Encapsulation of PCM by *in situ* polymerization includes two approaches where the capsule wall membrane can be formed from the inside and the other from outside of the core material by polymerization of monomers. The former approach has a drawback that only a limited number of suitable core materials can be used, because polymerization of polyisocyanates are necessary to obtain good wall membranes in the capsule. In the latter process, amino resins are generally used for the formation of encapsulating membrane. The mechanical strength of microcapsules made of melamine-formaldehyde (MF) resin[5] is found to be significantly greater than that based on urea. Therefore, *in situ* polymerization of MF is an important approach for making PCM microcapsules for textile applications.[6,7]

Another important requirement for such applications is to produce microcapsules with a very high PCM content as the core. This would help in reducing the overall weight of the fabric for a required capacity of heat storage. However, it has been observed that increasing the core content leads to poor formation of walls, thereby decreasing the stability of microcapsules under use.

It is reported that high molecular weight and superior strength of MF resin can be achieved by producing hexamethylolmelamine during methylolmelamine formation.[8,9] The hexamethylolmelamine can be prepared by a combination of 1 mole of melamine and 8 moles of formaldehyde on heating. The hexamethylolmelamine thus prepared has very less water solubility when compared with other methylolmelamines. The hexamehylolmelamine is also the most stable one and its further condensation leads to high molecular weight melamine-formaldehyde (MF) resin.[8,9]

The microcapsules containing fragrant oil were synthesized via the *in situ* polymerization method using melamine-formaldehyde as a wall material.[10] The encapsulation efficiency and other physical properties were also analyzed by them with varying formaldehyde to melamine molar ratio from 2.3 to 5.5 and pH of emulsion system from 5.0 to 6.0. The resultant encapsulation efficiency of fragrant oil varied from 67 to 81%. They claimed that both pH and melamine and formaldehyde molar ratio have an effect on the separation of MF prepolymer, consequently on the morphology of the microcapsule and encapsulation efficiency.[10]

In this study, an attempt has been made to investigate the effect of various parameters on the core content (*n*-octadecane) and stability of MF resin microcapsules. The parameters used are the refinement of the formaldehyde-to-melamine (FM) molar ratio and core-to-wall ratio during the encapsulation process. The microcapsules so produced are then characterized for core content, encapsulation efficiency, and stability. These capsules are coated on a cotton fabric to produce thermoregulated fabric having high heat storage capacity.

EXPERIMENTAL

Materials

Melamine (97.5%) and *n*-octadecane (98%) were purchased from S.D. Fine Chem Limited, India. Formaldehyde (37–41 wt %), poly(vinyl alcohol) (PVA, MW 10,000), sulphuric acid (97–99%), sodium carbonate anhydrous, and cyclohexane (99%) were obtained from Qualigens Fine Chemicals, India. Sodium lauryl sulfate (SLS) was obtained from G.S. Chemicals Testing Laboratory and Allied Industries, India. All chemicals were used without any further purification. A plain woven cotton fabric having 108 ends per inch and 77 picks per inch of 134 gsm and a polyester fabric of 132 ends per inch and 80 picks per inch of 65 gsm were used for producing a sandwiched thermoregulated textile fabric. RAN 5000 was procured from Qualigens Fine Chemicals and diammonium hydrogen phosphate was supplied by Merck, India. The binder based on vinyl acetate and acrylonitrile copolymer was procured from Jubiliant Organosys Limited, India.

Preparation of microcapsules

The microencapsulated *n*-octadecane was prepared through *in situ* polymerization technique. The procedure included the synthesis of prepolymer solution, the preparation of emulsion, and the formation of shell material. Melamine-formaldehyde prepolymer was prepared by adding calculated quantity of formaldehyde and melamine in 200 mL of distilled water taken in a beaker. The pH of the mixture was adjusted to 8.5–9.0 using a 10% solution of sodium carbonate. The temperature was raised to 70°C while continuously stirring the mixture using a magnetic stirrer. As the mixture becomes transparent, indicative of the formation of MF prepolymer, the temperature was reduced to 40°C. To this, SLS was added as an emulsifier and stirred well. Then *n*-octadecane was added slowly over 30 min while stirring the mixture using a high shear mechanical stirrer at 3000 rpm. The PVA (water soluble form) as a protective colloid was added to the mixture, and the stirring was continued for an additional 30 min to obtain reaction emulsion mixture.

To facilitate encapsulation, the mechanical stirrer from the reaction emulsion mixture was replaced with a magnetic stirrer. The system pH was slowly reduced to 3.0 from initial point of 8.5–9.0, using 10% solution of sulphuric acid while the temperature was raised slowly to 70°C from 40°C. These conditions were maintained for an additional 2 h for the formation of capsules. Finally, the capsules were cooled down to room temperature, filtered, washed with distilled water at room temperature, and dried at 40°C in an air oven for 15 h, and at 100°C for 90 min.

Fabrication of thermoregulated fabric

The coating paste was prepared by blending binder, RAN 5000 as thickener, and diammonium hydrogen phosphate as curing agent (or catalyst) in distilled water. To this, the microcapsules were added and mixed well to get uniform mixture. The ratio of microcapsules and the binder paste was kept to 1 : 1.4. The mixture was first coated on the cotton fabric using a doctor blade. Then the coating was covered with polyester fabric, and the sandwiched configuration was cured at 120°C for 20 min.

Characterization of microcapsules

Core content

The core content of the PCM microcapsules was determined using a Perkin Elmer Differential Scanning Calorimeter (DSC) model DSC 7 with intracooler. The heating and cooling scans were carried out at the rate of ±10°C/min in the temperature range of 0°C to 60°C. The core content can be calculated as per the following equation:

$$\text{Core content } (\%) = \frac{\Delta H_m}{\Delta H_o} \text{ X } 100$$

where ΔH_m is the enthalpy of microcapsules (Jg^{-1}) and ΔH_0 is the enthalpy of *n*-octadecane.

Microcapsule stability to solvent wash

This apparently represents the percentage of perfectly formed microcapsules, i.e., capsules without micropores. The stability of capsules to solvent wash can be determined by calculating the ratio of the core content of the solvent washed microcapsules to that of the distilled water washed microcapsules expressed as a percentage.

For the solvent wash, 0.5 g of dried microcapsules were washed with the 15 g of cyclohexane (solvent for *n*-octadecane) for 10 min at the room temperature, and the stability was obtained from the following equation:

$$\text{Weight loss } (\%) = \frac{W_d - W_s}{W_d} \text{ X } 100$$

where W_d is the weight of dried capsules taken, and W_s is the weight of solvent washed capsules.

Encapsulation efficiency

The Encapsulation efficiency can be determined by the following formula as the ratio of the total amount of core content present in microcapsules and percentage, i.e., of the amount of the core material taken during encapsulation process expressed as:

$$\text{Encapsulation efficiency } (\%) = \frac{\text{Weight of core material in the dried microcapsules}}{\text{Weight of core material taken}} \times 100$$

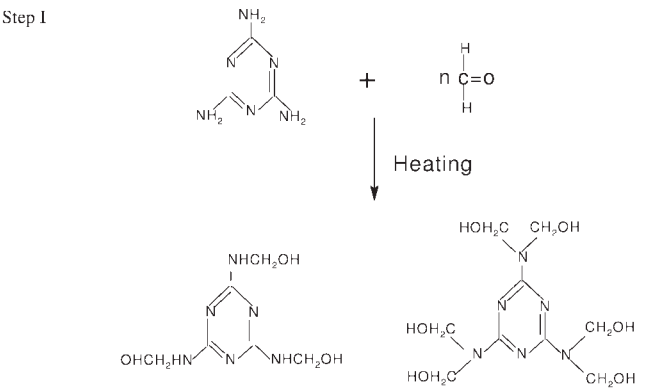
Microcapsule size and distribution

The size distribution of the microcapsules was determined by measuring diameters of 250 microcapsules under optical microscope.

RESULTS AND DISCUSSION

Effect of curing conditions on microcapsule properties

The mechanism behind the melamine-formaldehyde resin formation involves initially (Scheme 1; step I), the reaction between melamine and formaldehyde at a temperature of 65–70 °C, which leads to the formation of methylolmelamines. Depending on the relative amounts of melamine and formaldehyde used, the initial products can be di-, tri-, tetra-, penta-, or hexamethylolmelamines. On further heating, condensation of methylolmelamines takes place with liberation of water molecules and formation of ether linkages [step II (a)]. On subsequent reaction, these ether linkages may further convert to form methylene bridges with the liberation of formaldehyde [step II (b)]. Further heating of prepolymer in the presence of hydrogen ions turns the low molecular weight resin into a crosslinked structure as shown in step III. A fully cured and high molecular weight MF resin shows excellent resistant toward organic solvents.

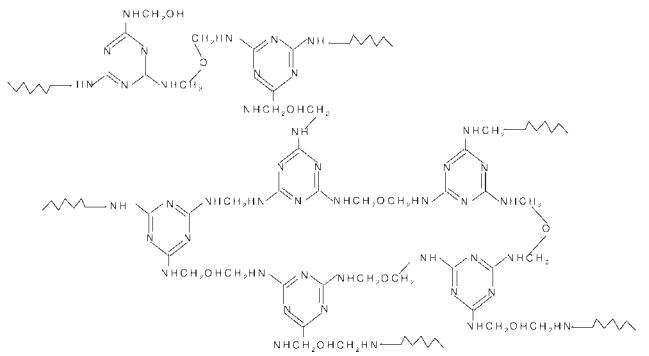


Step II

a) --$NHCH_2OH$ -- + --$HOCH_2HN$ -- → --$NHCH_2OCH_2NH$-- + H_2O

b) --$NHCH_2OCH_2NH$-- → --$NHCH_2NH$-- + CH_2O

Step III



Scheme 1

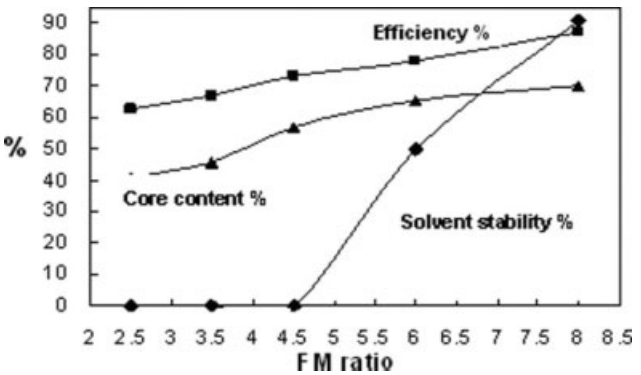


Figure 1 Effect of FM ratio on encapsulation efficiency, core content, and solvent stability.

The strength of wall material is important in case of encapsulation of PCM and thus influences the thermal and solvent stabilities. In the preparation of MF prepolymer, hexa-methylolmelamine is known to form in the presence of excess formaldehyde, i.e., 8 moles of formaldehyde for 1 mole of melamine on heating. In this particular case, the number of available reactive groups in melamine to react with the formaldehyde is low that results in slow condensation as compared with the low formaldehyde and melamine molar ratio. Heating leads to further condensation of hexa-methylolmelamine that eventually yields a high molecular weight melamine-formaldehyde resin. It is the most stable resin and had very less water solubility than the other methylolmelamines.

The strength of the wall material is influenced by the curing conditions, i.e., the temperature and pH profile of the encapsulation process. This ultimately controls the reaction when the condensation of MF prepolymer occurs and entraps the *n*-octadecane oil droplets. The encapsulation was initiated at 40°C by slowly lowering the pH in steps, and that resulted in slow condensation of MF prepolymer. The polymerized products were slowly deposited over the oil droplets. Then the temperature was increased to 45°C. Meanwhile the pH also reduced to 4 and maintained for sufficient time to allow the polymer particle to properly encapsulate the *n*-octadecane. To initiate the full condensation of all the available species of melamine and formaldehyde, the temperature was further increased to 70°C and pH brought to 3.

The microcapsules wall was again strengthened by controlling the temperature and time profile of curing conditions during drying. Curing results in the reaction of amine and methylol groups that are still available in the product. This reaction splits formaldehyde and forms strong methylene bridge. Thus, the fully cured and high molecular weight MF resin was obtained. The curing for normal MF resin product is effective at 160°C for 20 min, but for PCM encapsulated MF resin capsules is preferred at 100°C for 90 min because these conditions prevents the leakage of *n*-octadecane.[11] In the present study, the curing conditions have been modified to release formaldehyde slowly, the condensation byproduct. The capsules were dried at 40°C for 15 h for slow condensation and the temperature was raised to 100°C and kept there for 90 min for full condensation. The size distribution of the microcapsule showed that the capsules are in a narrow range of distribution (between 1.5 and 6 μm) with the average size of about 3.5 μm.

Effect of FM molar ratio on core content, encapsulation efficiency, and solvent stability

It has been observed that by varying the FM molar ratio, the effect of capsule loading amount, encapsulation efficiency and solvent stability can be varied. The FM molar ratio was increased from 2.5 to 8 (Table I). Accordingly the core content also increased from 40.8 to 70.2 (Table II and Fig. 1). This observation can be ascribed to the fact that the increase in FM molar ratio increases the amount of formaldehyde to that of melamine used, but the total amount of monomers remains the same (i.e., with constant core-to-wall ratio of 2). During the condensation of

TABLE I
Samples of Microcapsules Prepared for the Optimization Process

Sample Code	Melamine		Formaldehyde		SLS (g)	PVA (g)	PCM (g)	Core to Wall Ratio(w/w)
	g	Mole	g	Mole				
F2.5c2	6.27	1	9.65	2.5	7.5	1.25	20	2
F3.5c2	5.46	1	11.67	3.5	7.5	1.25	20	2
F4.5c2	4.83	1	13.26	4.5	7.5	1.25	20	2
F6.0c2	4.12	1	15.08	6	7.5	1.25	20	2
F8.0c2	3.44	1	16.82	8	7.5	1.25	20	2
F8.0c1	3.44	1	16.82	8	7.5	1.25	10	1
F8.0c3	3.44	1	16.82	8	7.5	1.25	30	3
F8.0c3.5	3.44	1	16.82	8	7.5	1.25	35	3.5
F8.0c4	3.44	1	16.82	8	7.5	1.25	40	4

TABLE II
Effect of Formaldehyde-to-Melamine Molar Ratio on Core Content, Efficiency, and Solvent Stability

Sample Code	Core Content, %	Encapsulation Efficiency, %	Stability to Solvent Wash, %
F2.5c2	40.8	62.6	0
F3.5c2	45.9	66.8	0
F4.5c2	56.8	73.4	0
F6.0c2	65.1	78.2	49.8
F8.0c2	70.2	87.3	90.6

TABLE III
Effect of Core Material on Core Content, Efficiency, and Solvent Stability

Sample Code	Core Content, %	Encapsulation Efficiency, %	Stability to Solvent Wash, %
F8.0c1	66.3	68.5	88.4
F8.0c2	70.2	87.3	90.6
F8.0c3	73.4	84.7	79.3
F8.0c3.5	77.1	85.5	60.8
F8.0c4	75.7	85.1	59.2

methlolmelamine, formaldehyde evaporates to form methylene bridge that results in low amount of wall material, which is required to coat the oil particles at higher FM molar ratios. It has also been observed that the encapsulation efficiency increases as the FM molar ratio is increased. It is the result of increase of the core content and this increased the total amount of oil particles being encapsulated.

There was no stability to solvent wash for the samples at the FM molar ratios of 2.5, 3.5, and 4.5. This indicates that the wall material formed over the PCM is not properly cross-linked. In these samples, the majority of the species formed was trimethylolmelamines in the FM prepolymer process. This is less stable than the hexa-methylolmelamine. Hence further condensation leads to poor wall structure. The poor wall structure again supplements in the sense that at low FM molar ratios, the available reactive site in melamine is comparatively high and this also leads to faster condensation. The samples produced at FM molar ratios of 6 and 8 forms the hexa-methylolmelamine during the preparation of MF prepolymer. Further condensation on heating leads to slow release of formaldehyde that results in better cross-linked structure of MF resin with high molecular weight. Therefore, capsules obtained with the high FM molar ratios showed better stability to solvent wash. The microcapsules so obtained, using 1 mole of melamine and 8 moles of formaldehyde, have been studied for thermal stability and found that the microcapsules are stable up to a temperature of 100°C.

Effect of core material on core content, efficiency, and solvent stability

The effect of core material on microcapsules properties showed that when the core-to-wall ratio is increased from 1 to 3.5, the core content increases from 66.3% to 77.1% (Table III and Fig. 2). The initial increase in core content is attributed to the fact that the increase in core material for same content of wall material. Then capsules core content started to decrease on increasing the core-to-wall ratio above 3.5, indicating that available wall material was not sufficient for proper encapsulation of the oil (octadecane) particles. It has been observed that when the core-to-wall ratio is increased from 1 to 2 the encapsulation efficiency increases significantly. Again, increasing the core-to-wall ratio to 4, the encapsulation efficiency starts decreasing. In the Table III, the solvent stability of capsules showed almost a decreasing trend with the increase in core material and reaches to a minimum value of 59.2%. This suggests that with the increase in the core material, the surface of the oil particles (to be encapsulated) increases with constant amount of wall material at particular FM molar ratio.

Thermoregulation of the coated fabric

The thermoregulated fabric during the DSC study showed the heat storage capacity of 105 J/g in heating cycle at 32.7°C, and the same energy was released back during cooling cycle at 25.0°C at the scanning rate of ±3 °C (Fig. 3).

CONCLUSIONS

Highly stable microcapsules of *n*-octadecane were prepared by *in situ* polymerization technique. It has been found that when FM ratio was increased from 2.5 to 8 and with core-to-wall ratio 2, the encapsulation efficiency increases. The capsules produced with FM ratio of 8 and core-to-wall ratio of 2 have encapsulation efficiency of 87.3% and contains 70.2% of *n*-octadecane and shows stability of 90.6% for

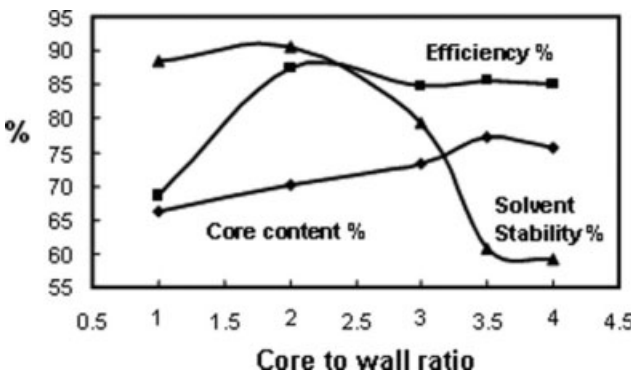


Figure 2 Effect of core materials on core content, encapsulation efficiency, and solvent stability.

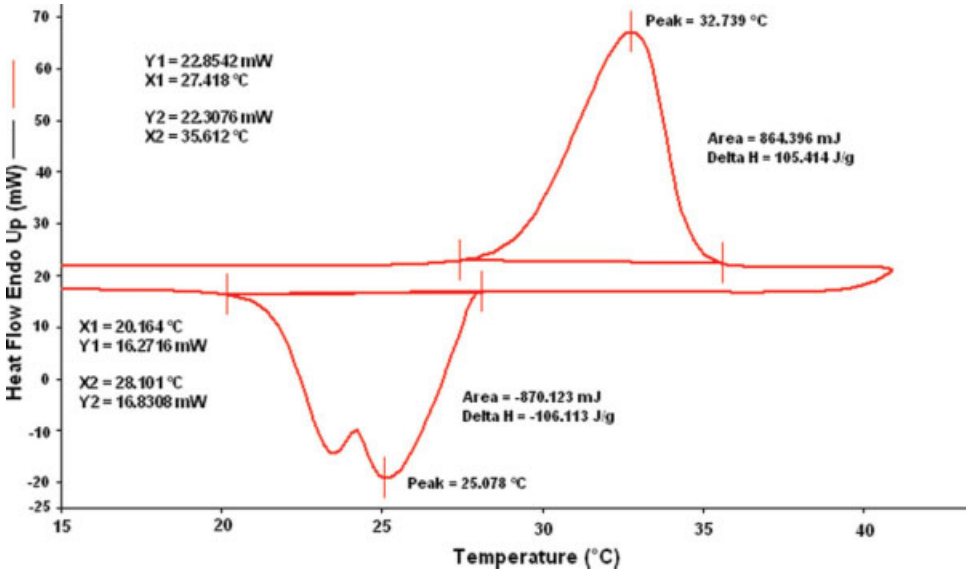


Figure 3 DSC micrograph of thermoregulated fabric in heating and cooling cycles. [Color figure can be viewed in the online issue which is available at www.interscience.wiley.com.]

solvent wash. The thermoregulated fabric produced has a heat storage capacity of 105 J/g. The above study shows that the suitable core-to-wall ratio lies between 2 and 2.5 with the FM molar ratio 8 to achieve capsules with high core content, efficiency, and thermal and solvent stabilities.

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