Effect of emulsion preparation method on microencapsulation of 
\(n\)-octadecane using melamine-formaldehyde pre-polymers

M Palanikkumaran, Kishor K Gupta, Ashwini K Agrawal \(^a\) & Manjeet Jassal \(^b\)
Department of Textile Technology, Indian Institute of Technology, New Delhi, 110 016, India

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The microcapsules containing \(n\)-octadecane as the core material and melamine-formaldehyde resin as the wall material have been synthesized by \textit{in situ} polymerization method. A systematic study has been carried out to investigate the effect of the method used in the preparation of reaction emulsion mixture, and the curing conditions used during the encapsulation process on the properties of microcapsules. The microcapsules so obtained are characterized for their core content, encapsulation efficiency, mean particle size distribution, and thermal & solvent stability. Using the modified encapsulation process with a formaldehyde-to-melamine molar 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 are found to be stable at temperatures more than 80 °C and to cyclohexane wash.

\textbf{Keywords:} \textit{In situ} polymerization, Melamine resin, Microencapsulation, \(n\)-octadecane, Phase change material, Reaction emulsion mixture

1 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 active core material such as drugs, proteins, antimicrobial agents, hormones, dyes, fragrances, flame retardants, phase change materials, etc can be used\(^{1-6}\). Generally, the wall materials are natural or synthetic polymers, metal or inorganic oxides suitable for particular end application. The potential applications\(^{2,7-10}\) of microencapsulation in textile finishing include insect repellent, aroma, antimicrobial agent, antibiotic, polychromic, thermochromic, cosmetic textiles, flame retardant finishes and many more. 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 materials that change their phase 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\(^{10-15}\).

Suitable PCMs that satisfy the major requirements of thermoregulation for application in textile clothing are \(n\)-octadecane, \(n\)-Eicosane and lithium nitrate tri-hydrate\(^{15-17}\). The material \(n\)-octadecane is particularly important because its melting temperature is very close to the comfort temperature of the body (around 28-29 °C) and it has a high latent heat of fusion (240 J/g)\(^{17,18}\). 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 drugs, perfumes, etc. that are present as core.

Encapsulation of PCM by \textit{in situ} polymerization refers to the polymerization of monomers from the same phase. This includes two approaches, namely (i) the capsule wall can be formed from inside and (ii) the capsule wall is formed 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. Therefore, generally the \textit{in situ} polymerization with monomer coming from continuous phase is preferred. In this process, amino resins, like urea-formaldehyde and melamine-formaldehyde, are generally used for the

\(^{a,b}\) To whom all the correspondence should be addressed.
E-mail: \(^{a}\)ashwini@smita-iitd.com, \(^{b}\)manjeet.jassal@smita-iitd.com
formation of encapsulating membrane\textsuperscript{19-21}. The mechanical strength of microcapsules made from melamine-formaldehyde (MF) resin is found to be more significant than that based on urea. Therefore, \textit{in situ} polymerization of MF is an important approach for making PCM microcapsules for textile applications\textsuperscript{20,21}.

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 methylol-melamine formation\textsuperscript{22,23}. The hexamethylolmelamine can be prepared by the combination of one mole of melamine and eight moles of formaldehyde on heating. The hexamethylolmelamine thus prepared has very less water solubility when compared to other methylolmelamines. The hexamethylolmelamine is also the most stable one and further condensation leads to high molecular weight melamine-formaldehyde resin.

In this study, an attempt has been made to investigate the effect of various parameters on the core content (\textit{n}-octadecane) and stability of MF resin microcapsules. The parameters used are the refinements of the method for preparing reaction emulsion mixture, and curing conditions during the encapsulation process. The microcapsules so obtained are then characterized for core content, encapsulation efficiency and stability.

\section*{2 Materials and Methods}

\subsection*{2.1 Materials}

Melamine (97.5\%) and \textit{n}-octadecane (98\%) were purchased from S.D. Fine Chem Limited, India. Formaldehyde (37-41 wt \%), polyvinyl alcohol (PVA, Mw 10000), sulphuric acid (97-99\%), sodium carbonate anhydrous and cyclohexane (99\%) were obtained from Qualigens Fine Chemicals, India. Sodium lauryl sulphate (SLS) was obtained from G.S. Chemicals Testing Lab & Allied Industries, India.

\subsection*{2.2 Preparation of Reaction Emulsion Mixture}

Three different approaches have been followed for preparing melamine-formaldehyde pre-polymer and emulsion of \textit{n}-octadecane. These are described hereunder. The details of parameters used in microcapsules formation are given in Table 1.

\subsubsection*{2.2.1 Addition of Pre-polymer to Prepared PCM Emulsion – Method 1}

In this method, the PCM emulsion was prepared first. Distilled water (200 ml) was taken in a beaker and the fine powder of SLS was added to this as an emulsifier followed by proper mixing. To this solution, \textit{n}-octadecane was added slowly over 30 min while stirring the mixture (the system temperature was maintained at 40 °C to avoid the solidification of PCM) vigorously 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 continued for an additional 30 min.

The MF pre-polymer was prepared separately by adding calculated quantity of formaldehyde and melamine in a beaker containing distilled water. The details of proportions of these materials for making the solutions are given in Table 1. Before heating the solution, the pH of the mixture was adjusted to 8.5-9.0 using 10 \% solution of sodium carbonate. The temperature was raised to 70 °C while continuously stirring the mixture using a magnetic stirrer. The mixture becomes transparent, indicating the formation of MF pre-polymer.

The MF pre-polymer, thus obtained, was added slowly into the prepared PCM emulsion and used for further process of encapsulation.

\subsubsection*{2.2.2 Addition of PCM Emulsion to Prepared Pre-polymer – Method 2}

In this method, the MF pre-polymer and PCM emulsions were prepared separately as described above. However, in this case, the PCM emulsion, thus obtained, was added slowly into the prepared MF pre-polymer and used for further process of encapsulation.

\subsubsection*{2.2.3 Preparation of Emulsion in Pre-polymer – Method 3}

Melamine-formaldehyde pre-polymer was prepared as described earlier by adding calculated quantity of formaldehyde and melamine (Table 1) in 200 ml of distilled water taken in a beaker. The pH of the mixture was brought to 8.5-9.0 using 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, indicating the formation of MF pre-polymer, the temperature was reduced to 40 °C. To this, SLS was added as an emulsifier and stirred well. Thereafter, \(n\)-octadecane was added slowly over 30 min while stirring the mixture vigorously 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.

### 2.3 Microencapsulation Process

To facilitate encapsulation, the mechanical stirrer from the reaction emulsion mixture was replaced with a magnetic stirrer. The \(pH\) of the system was slowly reduced to 3.0 using 5 % solution of sulphuric acid, while the temperature was raised slowly to 70°C. These conditions were maintained for an additional two hours 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, or at 100 °C for 90 min.

### 2.4 Characterization of Capsules

#### 2.4.1 Core Content

The core content of the PCM microcapsules was determined using a Perkin Elmer differential scanning calorimeter (DSC) (Model DSC 7) with intra-cooler. The heating and cooling scans were carried out at ±10 °C per minute between 0 °C and 60 °C. The core content was calculated using the following equation:

\[
\% \text{ Core content} = \frac{\Delta H_m}{\Delta H_0} \times 100
\]

where \(\Delta H_m\) is the heat of fusion of the microcapsules containing PCM in J/g; and \(\Delta H_0\), the heat of fusion of pure PCM in J/g.

#### 2.4.2 Microcapsule Stability to Solvent Wash

This apparently represents the percentage of perfectly formed microcapsules, i.e. capsules without micropores. This was determined by calculating the ratio of the core content of the solvent-washed microcapsules to that of the distilled water-washed microcapsules expressed in percentage.

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

\[
\% \text{ Mass loss (solvent wash)} = \frac{M_i - M_0}{M_i} \times 100
\]

where \(M_i\) is the initial mass of distilled water-washed microcapsules; and \(M_0\), the mass of solvent-washed microcapsules.

The stability of microcapsules to hot water wash was also determined in a similar way. For the hot water wash, 0.5 g of dried microcapsules was washed with 50 g of hot water for 10 min at 60 °C and the stability was determined using the following relationship:

\[
\% \text{ Mass loss (hot water wash)} = \frac{M_i - M_j}{M_i} \times 100
\]
where $M_i$ is the initial weight of distilled water-washed microcapsules; and $M_f$, the mass of hot water-washed microcapsules.

### 2.4.3 Encapsulation Efficiency (PCM Yield)

This is determined as the ratio of the total amount of core content present in all microcapsules and the amount of the core material taken during encapsulation process, expressed in percentage. The following equation was used:

\[
\text{% Encapsulation efficiency} = \left( \frac{M_1}{M_2} \right) \times 100
\]

where $M_1$ is the mass of core material in dried microcapsules; and $M_2$, the mass of core material taken.

### 2.5 Surface Morphology and Size Distribution

Scanning electron microscope (SEM) of the make Cambridge Instruments (model Stereo scan 360) and optical microscope by Leica model TK-C1380E were used to study surface morphology and size distribution. A drop of microcapsule dispersion was placed on sample stub, dried and coated under vacuum with silver for SEM studies. The size distribution of the microcapsules was determined by measuring diameters of 250 microcapsules under optical microscope.

### 3 Results and Discussion

The primary aim of this study is to investigate the effect of encapsulation procedure and curing conditions on core content, encapsulation efficiency and stability of the microcapsules. The results are given in Table 2. At the formaldehyde-to-melamine ratio of 3.5, the core content and encapsulation efficiency of microcapsule obtained from three different methods are found to be almost the same. However, the capsules are found to be unstable to solvent wash. This is because at the formaldehyde-to-melamine ratio of 3.5, majority of the melolmMelamines species expected during MF prepolymer preparation is trimethylolmelamines. This wall structure on further curing gives poor microcapsule stability to solvent wash. But stability of the capsules to hot water wash at 60 °C is quite good, except for the case when emulsion is added to the pre-polymer (Method 2). The microcapsules obtained, when the PCM emulsion is made inside the MF pre-polymer mixture (Method 3), show relatively better stability. This suggests that most appropriate method to produce the reaction emulsion mixture is to make the PCM emulsion inside the MF pre-polymer reaction mixture.

It is reported that high molecular weight and superior strength of MF resin can be achieved by producing hexamethylolmelamine during methylolmelamine formation\(^{24}\). Therefore, three different methods of preparing reaction emulsion mixture have also been studied with the composition of one mole of melamine and eight moles of formaldehyde. The results so obtained are shown in Table 2.

Again, the microcapsules obtained, while making the PCM emulsion inside the MF pre-polymer reaction mixture (Method 3), show relatively better properties. This can be ascribed to the fact that while making the PCM emulsion inside the MF pre-polymer reaction mixture, the discontinuous phase n-octadecane is well dispersed in the continuous MF pre-polymer phase, and the sufficient time is available for this dispersion. This method helps in

<table>
<thead>
<tr>
<th>Method of addition</th>
<th>Core content</th>
<th>Encapsulation efficiency</th>
<th>Stability to hot water (60 °C) wash, %</th>
<th>Stability to solvent wash at room temperature, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Core-to-wall ratio, 2]</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>3.5(^a)</td>
<td>3.5(^a)</td>
<td>8(^a)</td>
<td>8(^a)</td>
</tr>
<tr>
<td>Pre-polymer into emulsion</td>
<td>48.2</td>
<td>74.9</td>
<td>81.4</td>
<td>91.4</td>
</tr>
<tr>
<td>Emulsion into pre-polymer</td>
<td>47.2</td>
<td>74.5</td>
<td>65.1</td>
<td>87.6</td>
</tr>
<tr>
<td>Emulsion in pre-polymer</td>
<td>50.1</td>
<td>75.4</td>
<td>86.3</td>
<td>98.7</td>
</tr>
</tbody>
</table>

\(^a\) Formaldehyde-to-melamine ratio.

\(^b\) For Formaldehyde-to-melamine ratio of 3.5.

\(^c\) For Formaldehyde-to-melamine ratio of 8.
encapsulation by *in situ* polymerization of melamine and formaldehyde. *In situ* encapsulation of *n*-octadecane droplets occurs at a particular situation when MF pre-polymer further polymerizes to give the high molecular weight resin. Therefore, this method entraps (or encapsulates) the *n*-octadecane droplets better and eventually results in the good capsule geometry. However, in case of other two methods, either the MF pre-polymer is added to PCM emulsion (Method 1) or PCM emulsion is added to the MF pre-polymer (Method 2); both the methods of addition disturb the dispersion of oil droplets (oil phase) in water (aqueous phase) and finally the reaction emulsion mixture system. The microcapsules obtained by the method of making PCM emulsion inside the MF pre-polymer have also been studied for thermal stability, and it is found that the capsules are stable at temperatures more than $80$ °C.

The micrograph of the capsules obtained by optical microscope shows that the capsules are almost circular with a perfect periphery. It has been observed by SEM that the capsules are fused together. This may be due to the aggregation of the capsules at high curing temperature of $100$ °C (Fig. 1). The size distribution of the microcapsules shows that the capsules are in a narrow range of distribution (between $1.5\,\mu m$ and $6\,\mu m$) with the average size of about $3.5$ microns (Fig. 2).

### 4 Conclusions

The microcapsules prepared using the third method, i.e. the preparation of emulsion in pre-polymer, show relatively better properties and are found to be stable even at a temperature of $80$°C. Among the three methods, this method is most suitable for the encapsulation process.

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### References