Core Content and Stability of *n*-Octadecane-Containing Polyurea Microencapsules Produced by Interfacial Polymerization

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ABSTRACT: Microencapsulation of phase change material (PCM) *n*-octadecane was carried out by interfacial polymerization technique using core and bulk monomers as toluene-2,4-diisocyanate (TDI) and diethylene triamine (DETA), respectively. Cyclohexane was used as the solvent for TDI and *n*-octadecane, which formed the oil phase. The effect of encapsulation procedure, core-to-monomer ratio (CM ratio) and PCM-to-cyclohexane (PC) ratio was investigated on core content, encapsulation efficiency, and stability of microcapsules. Using a modified procedure, the core content was found to increase with the increasing CM ratio and reached a maximum at 3.7, while the encapsulation efficiency continuously decreased with the increasing CM ratio. Also the encapsulation efficiency was found to have a strong dependence on PC ratio and a maximum encapsulation efficiency of 92%, along with the core content of 70% was obtained with CM ratio of 3.7 along with the PC ratio of 6. The microcapsules were well shaped, i.e., round and regular, with narrow size distribution at these conditions. The PCM microcapsules were found to be stable to heat treatment at 150°C for 8 h. J Appl Polym Sci 106: 786–792, 2007

Key words: microencapsulation; polyurethanes; *n*-octadecane

INTRODUCTION

Encapsulation is a process of enclosing an active agent in a polymeric shell. The active agent can be in the form of a solid, a liquid, or even a gas, whereas, the wall material can be an organic polymer, hydrocolloid, sugar, wax, fat, metal, or inorganic oxide. The capsules are classified as microcapsules[1] if the particle size is <1000 μm. Microencapsulation by interfacial polymerization technique is one of the important techniques among many others reported in the literature.[2]

Some applications of microencapsulated products include carbonless copying paper, fire extinguishing compounds, adhesives, perfumes and fragrances, finishes for textiles, washing powders, medicinal products, insecticides, cosmetics, fertilizers, and so forth, where the particle size is in order of microns.[3]

One of the potential applications of microencapsulation is development of thermoregulated textile by encapsulating phase change materials (PCMs) for performing functions such as thermal storage and thermal regulation.[2–10] The core content of the microcapsule decides its capacity to perform the above functions. This capacity is measured in terms of J/g of capsules. In contrast to the above applications of microcapsules, where the core is expected to be released in solvent, under heat or under pressure, the microcapsules containing PCM must be stable to washings, heat, and pressure with the high core content.

Recently, there have been a few attempts[2,3] in encapsulating appropriate PCM such as octadecane using interfacial polymerization. Cho et al.[3] microencapsulated *n*-octadecane by interfacial polymerization of toluene-2,4-diisocyanate (TDI) and diethylene triamine (DETA). TDI was taken in oil phase (i.e. octadecane with cyclohexane), which was dispersed by emulsification in aqueous medium containing DETA. As the reaction conditions were attained, microcapsules were formed because of creation of polymeric wall at the interface of the oil droplet and aqueous phase. The authors used core versus monomer concentration of 3 g TDI for 20 mL of oil (octadecane + cyclohexane) and achieved a maximum core content of 46% with the encapsulation efficiency of 75%. The authors investigated the mechanism and kinetics of polymerization, and produced microcapsules of <1 μm in size suitable for incorporation into fibers.

Ni et al.[2] microencapsulated liquid paraffin by the same interfacial polymerization technique with an octadecane-to-cyclohexane ratio of 1. They used low core versus monomer concentration of 1 g for 12 mL oil and studied the effect of emulsification time and

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stirring speed on the reduction of microcapsule diameter. The core-versus-monomer ratio was considerably less in this study compared with that of the above study.

For applications in thermoregulated textile, it is important to maximize heat storage capacity per unit weight of microcapsules so that the increase in weight of clothing is mainly due to the PCM and not much due to the passive polymeric walls. Also, encapsulation efficiency and yields are important from the point of view of economics of such a process. It is known that increasing core content often leads to improperly formed walls around capsules, which leads to their low stability under heat. In polyurea encapsulation, cyclohexane is used possibly to facilitate diffusion of TDI monomer from inside of the core to interfacial region for efficient polymerization. However, the presence of cyclohexane along with PCM in the oil phase eventually reduces the PCM in the microcapsules, and therefore, the excess of it is undesirable. The significance of cyclohexane in microencapsulation process requires further investigation.

Recently, there has been a great emphasis on improving the core content and the thermal stability of the microcapsules formed using *in situ* polymerization of melamine formaldehyde and related systems.[11,12] However, such studies are not available in the literature for encapsulation through interfacial polymerization.

There is clearly a need to investigate how the core content, encapsulation efficiency and stability of polyurea microcapsules that are produced using interfacial polymerization may be improved. In this article, an attempt has been made to study the effect of encapsulation procedure and parameters, such as core-to-monomer (CM ratio) and PCM-to-cyclohexane ratios (PC ratio), on the properties of encapsulated *n*-octadecane.

EXPERIMENTAL

Chemicals

n-Octadecane, diethylene triamine, and ethylene diamine were purchased from S.D.Fine-Chem, Mumbai; toulene-2, 4 -diisocyanate, cyclohexane, and dibutyl tin dilaurate were purchased from Merck, Mumbai; and NP9.5, surfactant, was purchased from SS Dyechem, Delhi.

Preparation of microcapsules

Toluene-2,4-diisocyanate (TDI), cyclohexane, and *n*-octadecane were taken in a conical flask per the composition given in Table I. The mixture was then stirred at 500–1000 rpm on a magnetic stirrer plate for 5–10 min. The above mixture (oil phase or core material) was added to a 150 mL of aqueous solution of 0.5% NP-9.5 surfactant taken in a 250-mL beaker. The oil-in-water emulsion was formed by stirring the mixture at 2500 rpm using a high shear mechanical stirrer consisting of a mesh plate encasing the stirrer blades. Dibutyl tin dilaurate (2–3 drops) followed by 1.5 g of diethylene triamine (DETA) dissolved in 20 mL of water were added slowly to the emulsion while the stirring was continued to initiate the interfacial polymerization. The microencapsulation was carried out at the stirring speed of 2500 rpm for 5 min at the room temperature; thereafter the stirrer speed was reduced to 1800 rpm while the temperature of the mixture was raised to 60°C. The reaction mixture was maintained at these conditions for an additional

TABLE I
The Composition Used for Preparation of Microcapsule-Containing *n*-Octadecane

Core-to-monomer (CM) ratio (wt. ratio)	PCM-to-cyclohexane (PC) ratio (vol. ratio)	Monomers[a] (gm)	*n*-Octadecane (PCM) (gm)	Cyclohexane (gm)
6.5	1	2.2	7.5	6.9
3.6	1	4	7.5	6.9
3.2	1	4.44	7.5	6.9
2.4	1	6	7.5	6.9
7.4	3	2	11.25	3.45
3.7	3	4	11.25	3.45
2.5	3	6	11.25	3.45
1.8	3	8	11.25	3.45
3.60	1	4	7.5	6.9
3.65	2	4	10.0	4.6
3.68	3	4	11.3	3.5
3.71	6	4	12.9	2.0
3.73	12	4	13.8	1.1
3.75	no cyclohexane	4	15.0	0.0

[a] Assumed that only 1 gm of DETA is consumed for every 3 gm of TDI (per Ref. 3).

45 min. Thereafter, a second dose of 1.5 g of DETA dissolved in 20 mL of water was added to the above reaction mixture to increase the concentration of DETA. This helps in further diffusion of the monomer DETA through the capsule wall and supports further polymerization. The reaction was continued for another 45 min, the microcapsules were filtered, washed thoroughly in distilled water at 60°C to remove the unused monomers and core material, filtered again, and dried at 40°C for 12 h in an air oven. The above-mentioned hot water wash was found to be sufficient to remove physically trapped octadecane from the improperly formed microcapsules.

Characterization of microcapsules

Core content

The core content of microcapsules (C_a) is defined as the ratio of the heat of fusion (ΔH_m, J/g) of the microcapsules to the heat of fusion (ΔH_{PCM}, J/g) of the pure PCM (*n*-octadecane) expressed as a percentage.

$$C_a = \left(\frac{\Delta H_m}{\Delta H_{PCM}}\right)100$$

The heat of fusion or melting of the microcapsules was determined using Perkin–Elmer DSC 7 attached intra cooler. The samples were scanned at a rate of 10°C/min under N_2 atmosphere.

Theoretical core content

The theoretical core content (C_t) can be expressed as the ratio of the weight of PCM (W_{PCM}) to the combined weight of PCM (W_{PCM}) and monomers (W_m) taken for microencapsulation, expressed as a percentage.

$$C_t = \left(\frac{W_{PCM}}{W_{PCM} + W_m}\right)100$$

Encapsulation efficiency

The encapsulation efficiency (E) can be defined as the ratio of the actual core content of the microcapsules to the theoretical core content expressed as a percentage.

$$E = \left(\frac{C_a}{C_t}\right)100$$

Size and its distribution

Aqueous dispersion of microcapsules was placed on a glass slide, dried, and studied under Lieca optical microscope (LEICA DMLP) using JVC color video camera (TK-c1380). The mean particle size and its distributions were determined by measuring 250 capsules.

Surface characteristics

The microcapsules were sputter coated with silver and the morphology was observed under scanning electron microscope (Cambridge instruments SEM, STEREOSCAN 360). Since the PCM microcapsules could not be coated under high vacuum, a separate batch of microcapsules was produced using the modified method and only cyclohexane as the core material. Subsequently, cyclohexane was allowed to evaporate before carrying out the SEM analysis.

Stability of microcapsules

Heat stability of the microcapsules was evaluated by keeping the microcapsules wrapped in a tissue paper inside an air oven at 80–150°C for 8 h. The leakage of PCM from microcapsules was qualitatively determined by the amount of stains left by PCM on the tissue paper.

For the solvent stability (S), one gram of microcapsules was washed with 20 mL of cyclohexane at the room temperature for 10 min. The stability to the solvent was is defined as the ratio of the core content after solvent wash (C_s) to the core content before solvent wash (C_a), expressed as percentage:

$$S = \left(\frac{C_s}{C_a}\right)100$$

The core contents were determined by measuring the heat of fusion of the washed and unwashed microcapsules by DSC per the procedure given earlier.

RESULTS AND DISCUSSION

Agglomeration of microcapsules during encapsulation and their poor process stability to heat were the main problems during our initial attempts to produce microcapsules. To overcome these problems, various process parameters such as stirring speed during emulsification and encapsulation, encapsulation temperature and time, addition of catalysts were studied. According to reported method, emulsification of oil in water is carried out at high stirring speeds. The stirring speed is then reduced and second monomer is added to allow formation of wall around the emulsified oil droplets. At lower stirring speed during emulsification (500 rpm), the oil in water emulsion was found to be unstable and lead to coalescence of oil drops. Increasing the stirrer speed to 2500 rpm and above gave a stable emulsion. The effect of stirring speeds to give small capsules is reported in the earlier studies.[3] However, the problem of capsule agglomeration and poor stability still persisted even with the increased stirring speeds of up to 3000 rpm. Increasing the encapsulation temperature from 60 to

90°C, encapsulation time from 1 to 3 h, and adding dibutyl tin dilaurate to catalyze the interfacial reaction between the monomers TDI and DETA helped the polymerization process but could not solve the above problems. It is reported[13,14] that the use of dibutyl tin dilaurate helps in curing of wall at room temperature which improves the stability of the microcapsule. Eventually, the problem was traced to lowering of the stirring speed before the addition of the second monomer DETA. It was found that by reducing the emulsification stirring speed, a few minutes (5 min) after the addition of DETA, solved both the problems of capsule agglomeration and their poor stability to heat. This modification, which has not been reported in the literature, was found to be necessary and important in the preparation of microcapsules. The wall formation was better at lower speeds because the newly formed capsule walls did not rupture at low shear rates. However, it was also observed that when the stirring speed was reduced before or immediately after adding the second monomer, the droplets again tend to coalesce yielding to poor capsule formation. With these observations, it was inferred that while it was necessary to reduce the stirring speed to prevent rupturing of formed capsules, it was also necessary to allow short time for the initial wall layers to deposit at the high stirring speeds before lowering the stirrer speed. If the speed was reduced before the formation of the initial wall formation, the droplets tend to coalesce under low stirring speed and form deformed unstable capsules.

Effect of core-to-monomer ratio

The values of the actual core content and theoretical core contents are plotted against the core-to-monomer ratio (CM ratio) used during encapsulation in Figure 1(a,b). Here core content is defined as the amount of octadecane (PCM) in the final microcapsules, while the core in CM ratio during encapsulation procedure is the oil phase (i.e. sum of octadecane and cyclohexane). For one set of experiments, the PCM (which is octadecane) to cyclohexane ratio (PC ratio) was maintained at one while for another set it was maintained at 3. It can be seen from the Figure that at a high CM ratio, the actual core content is very low while the theoretical core content is at the maximum in both the cases. This suggests that the amount of monomer was not sufficient resulting in improper wall formation for the given amount of core material (both octadecane + cyclohexane). The loss of core material was very high at this stage. As the CM ratio was lowered, the theoretical core content decreases as expected, whereas the actual core content increased owing to a better wall formation around the core. The actual core content decreased after reaching a critical point at the CM ratio of 3.2 for PC ratio of 1 and 3.7 for PC ratio

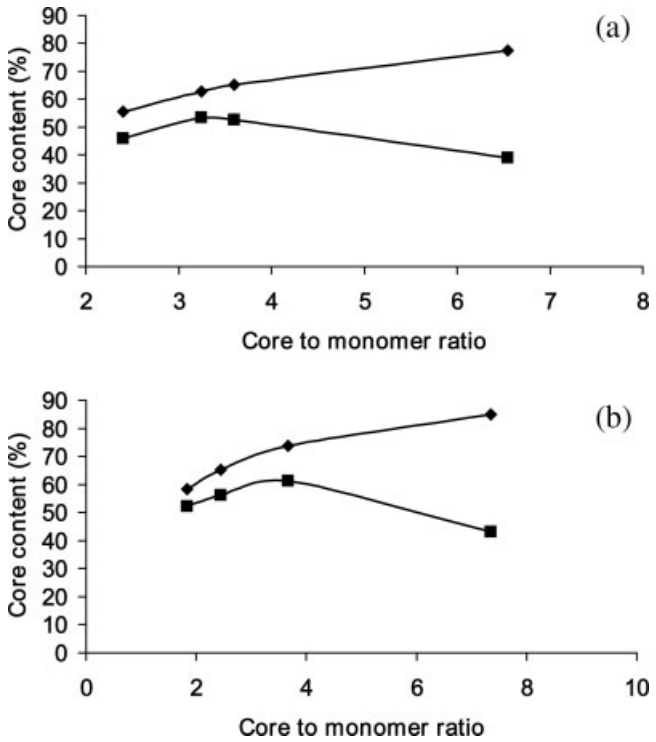


Figure 1 (a) Effect of CM ratio on core content of microcapsules prepared at PC ratio of 1; (◆) theoretical, (■) actual. (b) Effect of CM ratio on core content of microcapsules prepared at PC ratio of 3; (◆) theoretical, (■) actual.

of 3 indicating that CM ratio of 3–4 was sufficient to form stable wall around the core material. Any further increase in monomer content only adds the dead weight to the microcapsules, resulting in lower core content.

On the other hand, the encapsulation efficiency was very high at low CM ratio [Fig. 2(a,b)] because enough TDI is present in oil droplets to form proper polymeric walls.

Effect of PCM to cyclohexane ratio

The cyclohexane (a PCM solvent) along with the PCM (octadecane) is probably used for the better diffusion of core monomer (TDI) to the oil–water interface.[3] However, the amount of cyclohexane necessary for this phenomenon has not been investigated till now. It was important to minimize the use of cyclohexane to maximize the core content; however, reducing cyclohexane may have detrimental effect on the formation of walls due to poor diffusion of TDI within the core. Figure 3 shows the effect of PC ratio on core content of the microcapsules at CM ratio of 3.7. It can be observed from the figure that at low PC ratio, the core content is very low, that is, 52.63%, while it increases with the decrease in cyclohexane content, that is, increase of PC ratio. It can be inferred that decreasing the cyclohexane to a PC ratio of 6 inside the core did not affect the wall

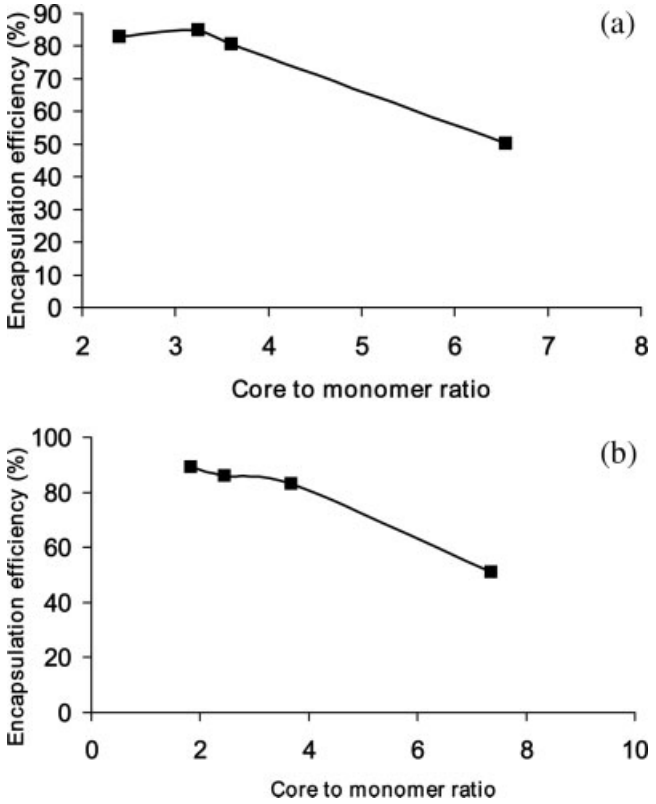


Figure 2 (a) Effect of CM ratio on encapsulation efficiency of encapsulation process at PC ratio of 1. (b) Effect of CM ratio on encapsulation efficiency of encapsulation process at PC ratio of 3.

formation. Therefore, the use of cyclohexane at very small concentrations (high PC ratios) was sufficient for the purpose of monomer diffusion. The core content above the PC ratio of 6 remained nearly constant, although, interestingly, highest value of 71% core was obtained when cyclohexane was not used in the core during encapsulation.

The plot of encapsulation efficiency against PC ratio is shown in Figure 4. The maximum encapsulation efficiency of 92% was obtained at the PC ratio of 6 while it was a little lower at PC ratio both below and above this value. This observation may be explained as follows. At lower PC ratio, the core would be less viscous and is likely to undergo shear deformation easily under experimental stirring speeds. On the other hand, at higher PC ratio, the viscosity of the oil phase (core) is likely to be so high that the monomer (TDI) is not able to diffuse effectively within the core leading to improper wall formation. Under both the conditions, core material was lost before encapsulation process was completed resulting in reduced encapsulation efficiency.

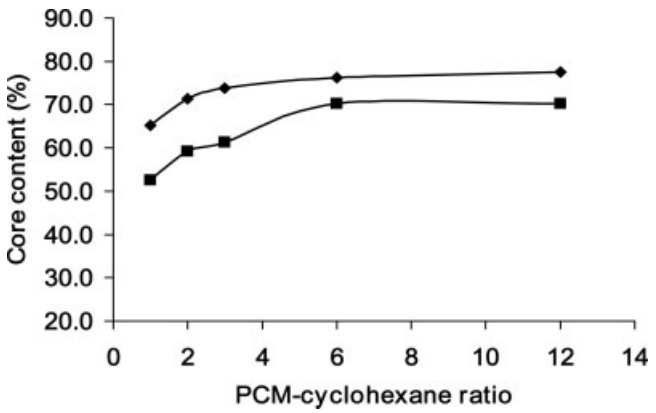


Figure 3 Effect of PC ratio on core content of the microcapsules prepared at CM ratio of 3.7; (◆) theoretical, (■) actual.

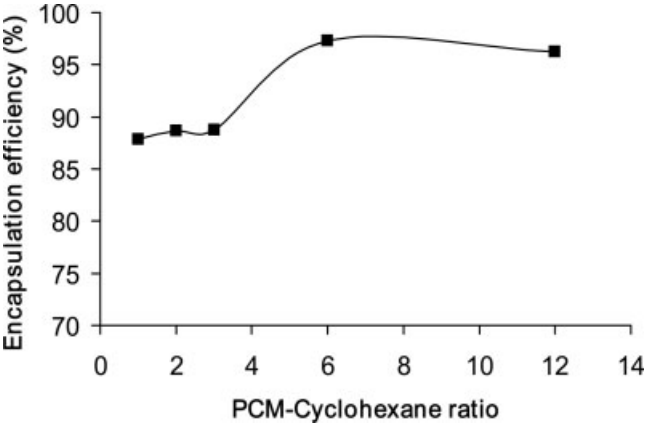


Figure 4 Effect of PC ratio on encapsulation efficiency of the microencapsulation process at CM ratio of 3.7.

Shape and size distribution

The size distribution of the microcapsules produced using CM ratio of 3.7 and PC ratios of 6 is shown in Figure 5. It can bee seen that most of the capsules clusters are below 10 μm; only a few microcapsules are between 10 and 14 μm, and none of them is above 14 μm. This variation in size appears to be because of the variation in the oil droplets formed during emulsification. The size and its distribution may be further improved by carrying out a better emulsification process. The average capsule size was calculated to be 7.3 μm.

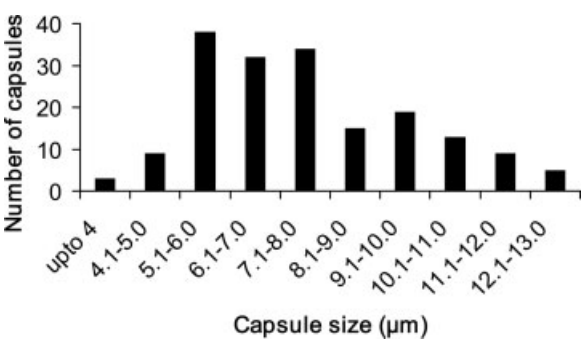
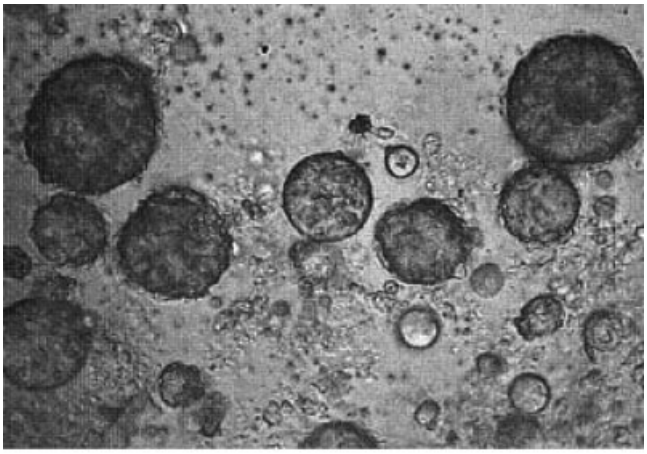
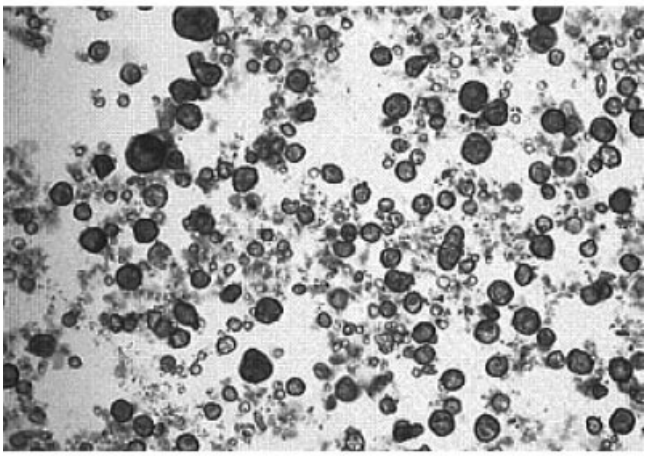


Figure 5 Microcapsule size and its distribution.



(a)



(b)

Figure 6 Optical micrographs of microcapsules produced from CM ratio of 3.7 and PC ratio of 6 at the magnification of (a) 500× and (b) 100×.

The optical micrographs of the microcapsules produced from the CM ratio of 3.7 with PC ratio of 6 are shown in Figure 6(a,b). It can be clearly seen that the capsules are formed even at very low amount of solvent in the core. The scanning electron micrograph of the microcapsules produced using cyclohexane as the core and CM ratio of 2.5 is shown in Figure 7. The size of microcapsules produced for SEM analysis using only cyclohexane was found to be significantly larger than PCM containing microcapsules. This may be explained on that fact that cyclohexane droplets may coalesce faster during encapsulation process due to their very low viscosity. However, these figures show that the capsules are well formed with round shapes using the modified encapsulation procedure.

Stability of PCM microcapsules

Stability to heat

The stability of the capsule to heat was tested at 150 °C for 8 h. The capsules were kept inside the oven inside the folded tissue paper. The leakage of the PCM to the tissue paper was tested. The capsules produced with the ''modified'' procedure (reducing stirring speed after 5 min of monomer addition) were found to be very stable, and did not leak at the above-mentioned conditions. In contrast, the microcapsules produced by reducing stirring speed before and immediately after addition of DETA were not stable at even much lower temperature of 80°C.

Stability to hot water wash

All capsules were washed with hot water at 60°C (well above the melting temperature of the PCM, which is 30°C) to remove physically entrapped *n*-octadecane with the improperly formed microcapsules. All the capsules produced with the modified procedure for microencapsulation were very stable to hot water wash and retained more than 95% of the PCM inside the capsule.

Stability to hot cyclohexane wash

The capsules produced with CM ratios of 1.8 and 2.5 at PC ratio of 3 (likely to have the stronger capsule walls due to the higher monomer amount with respect to the core); the capsules produced with core to monomer ratio of 3.7 at PC ratio of 6 (likely to have thinner wall) were tested for solvent stability. The selected capsules were washed with cyclohexane at room temperature to study the stability of the microcapsules to the solvent wash. The results obtained are tabulated in Table II. All capsules retained the core in the range of 35–55%, though; those with thicker walls were more stable. Cyclohexane being an excellent solvent for *n*-octadecane is likely to leach out the core from even well formed microcapsules.

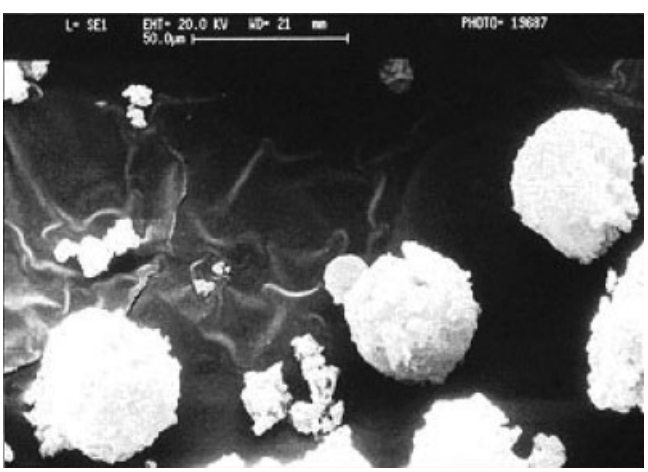


Figure 7 Scanning electron micrograph (SEM) of the microcapsules produced at CM ratio of 1.8 (without *n*-octadecane) at 20,000×.

TABLE II
Effect of Core-to-Monomer (CM) Ratio on Stability of Microcapsules to Cyclohexane (Solvent) Wash

Core-to-monomer (CM) ratio (wt. ratio)	PCM-to-cyclohexane (PC) ratio (vol. ratio)	Core content before cyclohexane wash (%)	Core content after cyclohexane wash (%)	Stability to solvent wash (%)
1.8	3	52.2	26.8	51.3
2.5	3	56.1	30.7	54.7
3.7	6	70.2	26.5	37.8

CONCLUSIONS

Microcapsules were produced by interfacial polymerization using toluene-2, 4-diisocyanate (TDI) and diethylene triamine (DETA) as monomers. The study of microencapsulation with various parameters was conducted to increase the core content with improved encapsulation efficiency and stability to heat and hot water wash.

From the initial experiments it was observed that the emulsification stirring speed of >2000 rpm was necessary for forming a good emulsion. It was found that the stirrer speed should be reduced to allow formation of continuous wall; however, the speed should not be reduced immediately after adding the aqueous phase monomer, DETA, to prevent capsule agglomeration.

The effect of core-to-monomer (CM) ratio and PCM-to-cyclohexane (PC) ratio was found to have profound effect on the core content, encapsulation efficiency, and capsule stability. The core content maximizes at a CM ratio of 3.7. Though the encapsulation efficiency was better at low CM ratios, it was reasonably high at 83% at CM ratio of 3.7. With the increase in PC ratio, both the core content and encapsulation efficiency was found to increase, although a small amount of cyclohexane as solvent (PC ratio 6) was found to help the microencapsulation process. The microcapsules produced with the CM ratio of 3.7, PC ratio of 6 gave the best microcapsules with core content of 70%, and encapsulation efficiency of 92%. The highest core content of 71% was obtained without using any cyclohexane at the CM ratio of 3.7.

The microcapsules were found to be stable to heat at 150°C for 8 h and repeated hot water wash. However, they were found to be only moderately stable to solvent wash. The microencapsulation with low CM ratios of 1.8 or 2.5 gave microcapsules with better stability to solvent wash than CM ratio of 3.7.

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