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Synthesis of Micro encapsuled Beeswax using in-situ polymerization and its characterization

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Abstract

Application of Phase Change Material (PCM) in micro form increases more latent heat energy compare to macro form. This paper focuses on the microencapsulation of Beeswax PCM as core material and Urea-formaldehyde as shell material for utilizing them in thermal management applications using their latent heat storage. The in-situ polymerization method was adopted for microencapsulation Beeswax to obtain better surface morphology and minimum size. The microencapsulated Beeswax was characterized Scanning Electron Microscope (SEM), and Fourier infrared spectroscopy (FTIR). The thermal stability was evaluated using a Thermogravimetric analyzer (TGA). From the SEM analysis average diametrical size for the microcapsules was 0.23 µm. Chemical availability Beeswax core material and urea formaldehyde shell material was verified from absorption peaks in FTIR test. The maximum temperature of microencapsulated Beeswax was 210℃. The dynamic temperature was verified using Differential scanning calorimetry (DSC), the maximum temperature in the microcapsule was 62.5 ℃, the cooling temperature was 59.7 ℃.

Keywords. Beeswax, In-situ polymerization, Latent heat storage, Microencapsulation, Thermal management.

1. INTRODUCTION

The conservation of energy can be accomplished in two ways: by judicially using all the electrical equipment and disconnecting devices on idle condition from the power supply. Generally, PCMs are fatty acids or wax material. These materials are highly capable of storing a large amount of thermal energy. However, most of

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the PCM are less thermally conductive. In order to improve the thermal conductivity, the surface area of PCMs needs to be improved. There are several other chemical methods to microencapsulate the PCMs [1], namely the sol-gel method, in situ polymerization, interfacial polymerization, suspension polymerization, complex coacervation, emulsion polymerization [2].

In the previous researches, many attempts done with Beeswax to use for latent heat storage by means of raw Beeswax in pouches and balls, Beeswax emulsion form, Beeswax with graphite, copper and silver nano particles for increasing thermal conductivity. The novelty of the present work is microencapsulated Beeswax using urea-formaldehyde as shell material. Since the previous researches reported that urea formaldehyde shell gives self-healing qualities to microcapsule while heating and also it improves encapsulation of the polymer shell [3].

In this paper, the in-situ polymerization method of microencapsulation is investigated for Beeswax. It is expected that the microcapsules obtained from this method will have better bonding strength [4]. The microencapsulated product is characterized for surface morphological analysis, functional group, and thermal behaviour.

2. MATERIALS AND METHODS

Beeswax ($C_{15}H_{31}COOC_{30}H_{61}$; melting temperature 64℃ and boiling temperature 85℃) was the PCM used in the study. Urea(CH_4N_2O – 99%) and formaldehyde (CH_2O – 37.4% w/v) were used as shell materials, as urea-formaldehyde rendered the shell with better thermal conductivity, i.e.,0.433 w/m℃ [5]next to water (k_{water} 0.599 w/m℃. Ammonium chloride was used as a nucleating agent, while sodium hydroxide (NaOH) and deionized water were used as general laboratory reagents. Hydrochloric acid (HCl) was used as an acidic liquid, and sodium hydroxide (NaOH) was used as a basic buffer for maintaining the pH level close to 5. Resorcinol ($C_6H_4(OH)_2$) was used as the crosslinking agent of microcapsules.

2.1. *Extraction of Beeswax Phase-Changing Materials*

Beeswax is extracted from a natural honeycomb. Initially, the honeycomb was collected and dried after removing the honey inside the individual holes. The powdered honeycomb was poured into the water, boiled at 100°C. For getting 100 g of Beeswax, 250g of honeycomb needs to be used. The water was maintained in the boiling state for 30 minutes. Then the melted wax started to float on the surface of boiling water. Once the liquid wax formed, it changed to a white or whitish-yellow colour, and the liquid was taken and filtered using a pure cotton cloth. Thus, the unwanted dust particles settled above the cloth. The water and melted wax were

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poured into the glass jar for cooling. The process flow chart for extracting Beeswax is shown in Figure.1.

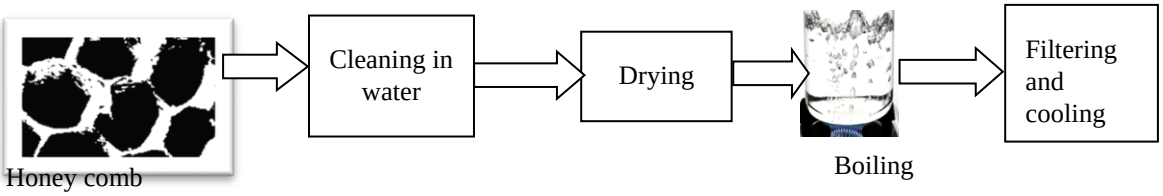

Figure.1 Stages of manufacturing Beeswax or Beeswax Phase-Changing Materials.

2.2. *Selection of Chemical Polymerization method*

The in-situ polymerization method was recommended for improved bonding and tightness. In-situ polymerization method, which uses water-oil emulsion of shell material, and covers the core material after certain chemical processes. If larger particles are made into a smaller particle by stirring operation, the smaller amount of core material will be covered by shell material, which will create new microencapsulated particles; this process is known as microencapsulation [6].

2.3. *Emulsification process*

2.5 wt. % of Ethylene malic anhydride emulsifier was prepared for 10g of PCM. About 250 ml of Ethylene maleic anhydride was used for preparing the emulsion, wherein it was poured into 250 ml of water and stirred at 500 rpm using a magnetic stirrer. Another container of 200 ml capacity was filled with distilled water, and 0.5 g of resorcinol, 0.5g of ammonium chloride, and 5g of Urea were added. Then, 10 ml of Ethylene maleic anhydride solution was taken, added to the mixture, and stirred at 500 rpm. Hydrochloric acid and sodium hydroxide solutions were added dropwise for maintaining the pH level of the solution at 5.

2.4. *Formation of Microcapsules*

The prepared emulsion solution was heated to 70 ℃ because the Beeswax melting temperature was 64℃. 10g of Beeswax was added to the solution, followed by 10ml of formaldehyde solution, while the pH was maintained between 5-7 by adding one or two drops of sodium hydroxide solution and hydrochloric solution, as per the requirement. The stirring speed was increased to 1000 rpm and maintained for 5 hours at a constant temperature of 70℃. A smooth surface finish and smaller size can be obtained by maintaining constant stirring speed [7]. The chemical operation of the process is given below in Eq.1.

$$C_{15}H_{31}COOC_{30}H_{61} + NH_4Cl + C_6H_4(OH)_2 + CH_4N_2O + HCHO$$

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$$\rightarrow (CH_3NH)_2CO + NH_4Cl + C_6H_4(OH)_2 + C_{15}H_{31}COOC_{30}H_{61} \quad (1)$$

3. RESULTS AND DISCUSSION

An examination and understanding of the characteristics of microencapsulated PCMs, such as shape, size, surface morphology is essential to determine their applicability. [9]. The SEM is used to observe the surface morphology, shape, and size; this will give the primary evidence of the formation of microcapsules. FTIR test was used to observe the functional groups of the chemical compounds formed in the microparticles. To assess the microcapsule's temperature stability, Thermogravimetric analysis (TGA) of the microcapsules was conducted [8].

3.1. *SEM Analysis and FT-IR analysis for microencapsulated PCM*

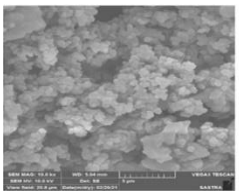

Fig. 2 (a)

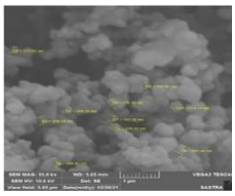

Fig. 2 (b)

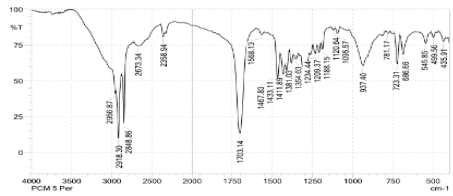

Fig. 2 (c)

Fig. 2 (a) and (b) SEM analysis 2 (c) FT-IR (Core, Shell, and microcapsule)

SEM test was done using ZEISS microscope. The fibrils were scanned for the different wavelength of the electron with different magnification varied from 100 X to 500 X, with the accelerated voltage of 20 KV. The images observed in the SEM are shown in Figs. 2 (a) and (b). From the SEM analysis, the shape of the microcapsules is spherical, as in-situ polymerization was used for microencapsulation. The maximum size observed in the microcapsule was 299.45 nm, while the minimum size of microcapsules measured in the image was 176.53 nm. The average diametrical size of the microcapsule was 0.23µm. The microcapsule surface had no dimples or depressions and exhibited a smooth texture.

FTIR test was done using SHIMADZU- instrument model (IR TRACER 100). The absorption peaks of Urea and the microcapsules were observed at 1020 cm^{-1} to 1250 cm^{1} attributed to the stretching vibration of the C-N group. Similarly, the absorption peaks of formaldehyde measure from 1685 cm^{-1} to 1710 cm^{-1}, which are observed as stretching bands of C=O bonds. Also, the peaks corresponding to the core material can be observed between 2500 cm^{-1} to 3000 cm^{-1}. This result shows the presence of Beeswax, urea, and formaldehyde in microcapsules.

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3.2. *Thermogravimetric analysis and Differential Scanning Calorimeter (DSC)*

A Thermogravimetric analyzer (TGA 4000, Pyris 6 machine) was used for this study. In this test, the temperature was increased, and the weight loss of the sample over the heating, holding, and cooling time was monitored. Fig. 4 a shows the TGA graph, where in the weight loss was gradual between 0 - 200 °C. At 210°C, there is a slight steep fall in the mass of the sample. Again, the mass loss was quite notable between 230°C and 350°C. Thus, the material began to decompose at 210°C. So, the maximum temperature the microencapsulated Beeswax can withstand without decomposition is 210 °C. Hence, the material can be operated within the regime of 0-200°C.

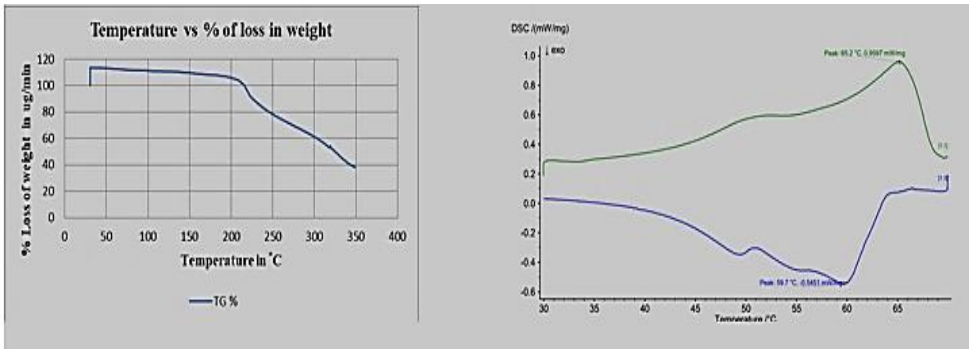

Figure. 4a TGA of microencapsulated Beeswax, Fig. 4b Heating and Cooling curve by DSC test.

In the DSC analysis the temperature was raised by about 10 ℃ until 350 °C cooled down to the initial temperature in the same manner. Fig. 4b shows the heat flow in the system during the heating-cooling of the microcapsule. The DSC results shows that the maximum heating temperature reached 65.2℃ and enthalpy verified about 0.9597 mW/mg and the cooling temperature peak attained 59.7℃ and enthalpy reaches 0.5451 mW/mg. So, the results revealed that usage of PCM for electronic component cooling can comfortly be done instead of air cooling done by fan.

4. Conclusion

Beeswax was successfully obtained from the honeycomb, and microencapsulation was done through the in-situ polymerization method. The microencapsulated Beeswax was spherical, smooth and the average size was between 0.2μm to 0.3μm. Chemical characterization of the encapsulated PCMs was conducted using FTIR spectroscopy to confirm the presence of PCMs in the Beeswax core material and Urea formaldehyde shell material. FTIR analyses

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confirmed the presence of Urea, formaldehyde, and the core materials with the peaks corresponding to their functional groups at 1020 cm^{-1} to 1250 cm^{-1},1685 cm^{-1} to 1710 cm^{-1}, and 2500 cm^{-1} to 3000 cm^{-1}. The maximum temperature of microencapsulated Beeswax before decomposition was 210 ℃. The cooling and heating curves of microencapsulated Beeswax were observed at 59 ℃, and 65.2 ℃. The microencapsulated Beeswax is used for latent heat storage systems for operating temperatures below 65 ℃. The future work is plan to do the nano encapsulated PCM.

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