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Synthesis of Microcapsules from Melamine Formaldehyde Encapsulated Lauric-Myristic Acid Eutectic for Cool Solvent-Based Decorative Coating

[1]Neeraj Pasarkar, [2]Mukesh Yadav, [3]Prakash A Mahanwar
Department of Polymer and Surface Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga (E), Mumbai, 400019, India

Abstract:- The goal of this work is to develop a prospective cool decorative coating used to store thermal energy with the use of melamine formaldehyde microcapsules containing core of a eutectic mixture of Lauric acid-Myristic acid as a phase change material. Melamine and formaldehyde were reacted in a two-step reaction to create the shell material. To be used in applications involving thermal energy storage, these microcapsules (0–15 weight %) were mixed with a red oxide primer basecoat and a white enamel topcoat system after centrifuging and drying. The Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Polarized Optical Microscopy (POM), and Scanning Electron Microscopy (SEM) techniques were used to analyse the microcapsules. LA-MA eutectic, incorporated in the microcapsule (MF-LA-MA), has been found to melt at C with the latent heat of melting 116.2J/g and crystallizes at with latent heat crystallization 114.4J/g. The phase change characteristics of the coated material were observed to improve as the microcapsule loading increased. The thermal energy transfer rate was enumerated in terms of the time taken by the coated panels to attain an equilibrium temperature of 60C. According to Thermogravimetric Analysis (TGA), LA-MA eutectic in the microcapsule has improved thermal stability.

Keywords:- *Phase Change Material, Thermal Energy Storage, Microencapsulation, Cool Coating.*

I. INTRODUCTION

Researchers have been encouraged to develop greener, sustainable technology as a result of growing climate change worries in order to lessen the environment's increasingly negative effects. The conservation of thermal energy is one of the topics that has received the greatest attention in this area. When undergoing a phase shift, substances known as phase change materials (PCMs) can store and release a significant amount of energy. PCMs have advanced significantly in the realm of thermal energy and are used in a variety of settings. In most cases, the solid PCM melts into the liquid phase when heated. The phase transition of PCMs is challenging from an application perspective because the PCM must be confined in order to avoid any leakage. Here, the PCM microencapsulation technology has been taken into consideration. Of course, there are numerous distinct methods used to stop leakage, with shape stabilization being the most crucial. Microencapsulation offers the advantage of preventing PCM leakage during phase change, speeding up heat transfer, regulating volume change during phase change, and preventing PCM reactivity with the environment. As a result, microencapsulation is seen to be the best method for preventing leakage. Both organic and inorganic shell materials can be used to generate microencapsulated phase change materials (micro PCMs). Due to its simplicity of production, polymer has become more popular as a shell material than inorganic shell materials. Performance and stability of Micro PCMs(Sharma et al., 2014) made of melamine formaldehyde resin, urea formaldehyde(Huo et al., 2020), polyurethanes, polyurea, and polymethyl methacrylate(Sari et al., 2015), among other materials, have been investigated. Paraffin compounds(Hong & Xin-shi, 2000) are the most often utilized PCMs because of their significant latent heat of melting, the insoluble nature in water, and chemical inertness.

Alkyd resin continues to be the resin of choice for many coating applications(Hong & Xin-shi, 2000). There are numerous applications for alkyd topcoat and alkyd primer, including coatings for metal and wood. The applications for alkyd enamel are numerous. It has good decorative features and vibrant hues. It has a wide range of applications for steel equipment and wood products. These coatings would prevent leaks and operate well over time if microencapsulated PCMs were added. Another aspect of this inquiry is examining the effect of microcapsules on the extent of corrosion. Temperature is just one of several factors that influence corrosion rate because of the electrochemical basis of the reaction. The increase in temperature on the metal surface can be actively reduced using PCMs. As a result, the substrate temperature will be regulated, and the pace of corrosion will be slowed. In order to minimize reliance on electric energy and decrease substrate corrosion, PCMs will thus serve a dual purpose.

To increase the thermal stability of micro PCMs, melamine-formaldehyde (MF)(H. Zhang & Wang, 2009) have employed as the shell in a variety of microcapsule applications. Because of their strong reactivity, quick response time, and great thermal stability, they have also been employed for PCM encapsulation. Microencapsulated

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PCMs have been investigated in PU foams(Konuklu et al., 2015) for applications in the textile industry(H. Zhang & Wang, 2009), coatings(Coatings, 2006), the preservation and transportation of temperature-dependent products, the thermal convenience of buildings(Kuznik et al., 2011), storing thermal energy in buildings, the textile industry, and other areas. Additionally, studies on the characteristics of micro PCMs in thermo-regulated fabric fibers(Konuklu et al., 2015), textiles, coatings as well as foams have been conducted.

In the current work, melamine formaldehyde (MF) is used as the shell material for the microencapsulation of a eutectic mixture of Lauric acid and myristic acid as PCM core. The microcapsules are then incorporated into the alkyd white enamel topcoat system. In a eutectic mixture (PCM)(Zhu et al., 2015), lauric and myristic acids were mixed to achieve higher latent heats of melting throughout a constrained limit of temperature with almost no super-cooling effects.

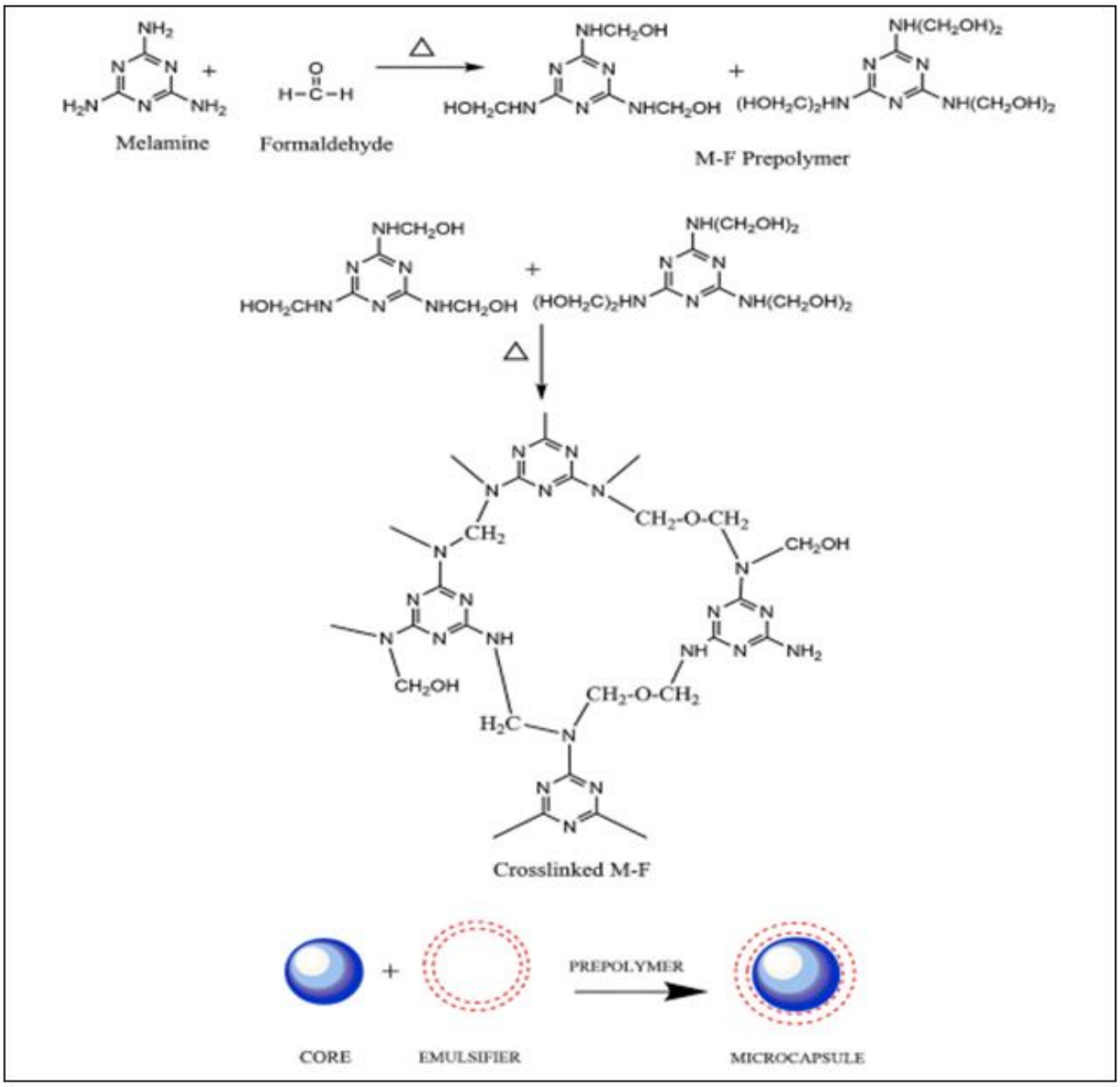

Fig 1 Formation of Melamine Formaldehyde and Synthesis of the Microcapsule.

II. EXPERIMENTAL

A. Materials

Lauric Acid (LA) and Myristic Acid (MA) were supplied from Sigma-Aldrich and its eutectic mixture was utilized as the phase change material. Melamine and formaldehyde (37% solution) were procured from Loba Chemicals Pvt. Ltd., Mumbai, India, and were used to make the polymeric shell of the microcapsule. Sodium Lauryl Sulphate (SLS), ordered from SD Fine Chemicals Pvt. Ltd., Mumbai, India was acted as a surfactant for the dispersion of LA-MA Eutectic Mixture in water. In order to alter the pH of the emulsion to an acidic and basic value, respectively, acetic acid (AA) and triethylamine (TEA) were acquired from SD Fine Chemicals Pvt. Ltd., Mumbai, India. For Alkyd enamel paint preparation, long oil alkyd resin (60%), titanium dioxide, methyl ethyl ketoxime (MEKO), soya lecithin, Bentone SD1, Mineral Turpentine Oil (MTO) driers such as zirconium octoate (18%), calcium octoate, and cobalt octoate (6%),were obtained from industry. Without any additional purification or treatment, all chemicals were utilized exactly as they were purchased.

B. Synthesis of Microcapsules using Phase Eutectic Mixture as Core and Melamine Formaldehyde as Shell Material

By mixing 66% lauric acid and 34% myristic acid, a phase eutectic combination with a temperature range of 34°C to 35°C was created. Two different flasks containing lauric acid and myristic acid were added, then melted. The samples were combined in a single flask while still in a liquid condition and swirled for roughly an hour using a hot plate magnetic stirrer. The resulting mixture was then cooled to room temperature before being examined for its ability to undergo phase changes.

An in-situ polymerization method(X. X. Zhang et al., 2004) was adopted to encapsulate LA-MA Eutectic. In the beginning, 60 mL of deionized water was poured into 500 mL round-bottomed flasks with three necks and an agitator and a condenser. 40 g of the LA-MA eutectic mixture were melted and added to a flask that had been preheated to 60 ± 2 °C. 1.64 g of SLS was added to this the blend, which was then sonicated at 70% amplitude for 15 minutes and agitated at 700 rpm at 60 ± 2 °C for an additional 15 minutes. After 30 minutes of rigorous mixing, acetic acid was employed to bring the pH level down to 4. In the meantime, a 100 mL beaker containing 10 mL of deionized water, 39 g (mol) of formaldehyde (37% solution), and 14 g (1 mol) of melamine was obtained and properly mixed using the magnetic stirrer. The solution was heated to 70 ± 2 °C. After a few minutes, the pre polymer mixture becomes transparent from its milky white colour. Regulate the pH to 8 using sodium hydroxide solution. Fig. 1 depicts the reaction process that results in the development of the MF-LA-MA Eutectic microcapsule. After 30 minutes of continuous agitation, the pre-polymer was added dropwise to the mixture in the round bottom flask. This process was then continued for 1.5 hours. The reaction was subsequently ended by bringing the pH to 9 using TEA. Following a 30-minute centrifugation of the combination, the leftover microcapsule mixture was gathered. To create the finished product, the microcapsules were subsequently dried at 80 ± 2 °C for 5 hours.

C. Preparation of MF Microcapsule Incorporated Long Oil Alkyd Based Enamel Paint:

As per the specified recipe, a long oil alkyd-based white enamel topcoat is produced. After drying, the micro PCMs were added to the white enamel topcoat(Naikwadi et al., 2020). At various weight proportions of 3%, 6%, 9%, 12%, and 15%, the particles were incorporated. Using a brush, the white enamel finish was then applied on metal panels that had been primed with red oxide. There was a discernible increase in coating thickness when the solid component of the coating rises with higher particle loading. Red oxide primer was dissolved in a 20% dilution of an MTO solvent. After that, the coated panels were given seven days to cure at room temperature. In accordance with the specified formulation, a long oil alkyd-based White Enamel Topcoat is created, and utilizing MTO as a solvent, an alkyd white topcoat with the micro PCMs loading is then applied. After that, the coated panels were given seven days to cure at room temperature. Following storage, the coated panels were analysed, and their performance was assessed. The basic formulation for long oil alkyd-based enamel paint is given below:

Table 1 Basic Formulation for White Gloss Enamel:

Raw Material	**% Weight Basis**
Long oil alkyd resin (LOA) (60%)	7
Soya lecithin	0.4
MTO	3.57
Bentone SD1	0.15
TiO_2	15
Stabilization	
LOA	18
MTO	10
Thinning	
Long oil Alkyd resin (60%)	28
MTO	15.08
Cobalt Octoate (6%)	0.4
Zirconium Octoate (18%)	0.6
Calcium Octoate (8%)	1.4
Methyl ethyl ketoxime (MEKO)	0.1
Defoamer	0.3

D. Characterization

To determine the functional groups in the microcapsule, polyester films were subjected to Fourier transform infrared (FTIR)(Konuklu et al., 2014) spectroscopy using a Bruker equipment in the ATR (attenuated total reflectance) mode. The thermal characteristics of the LA-MA Eutectic, MF-LA-MA Eutectic, and MF-LA-MA Eutectic/Long oil Alkyd systems were determined using differential scanning calorimetry (TA Q100 DSC analyser; TA instrument, USA). Using a nitrogen atmosphere, heating and cooling phases have been measured at a rate of 5 °C/min from 0 and 100 °C.

Utilizing solar thermal energy storage equipment, the solar thermal energy rate of the coated panel with and without microencapsulated particles was examined. This experiment's goal was to ascertain how long thermocouple TB took to attain its equilibrium temperature of 60 ± 2 °C. The rate of heating was 5 °C/min. A thermogravimetric analyser (TGA)(Sari et al., 2015) (PerkinElmer Pyris 1 TGA) was used to measure the thermal stability of LA-MA eutectic, LA-MA-MF, and LA-MA-MF integrated coatings under conditions of 30-600°C heating and 20 mL/min nitrogen purge. Decomposition temperature was determined to be the temperature at which the beginning weight loss occurred. The change in phase of the microcapsules was studied using an Olympus BX41 polarized optical microscope (POM)(Fang et al., 2010). SEM images of structural morphologies were collected using a Hitachi S-4700 SEM(He et al., 2016). In order to assess the coating system's coating hardness, ASTM D 3363 was used to measure the coating system's pencil hardness. The coated panels were bent over a conical mandrel in accordance with ASTM D 522 to assess the coatings' flexibility and crack-resistance. In order to determine scratch resistance, the ISO 104 technique was used. According to ASTM D 117, the

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coated panel performed a salt spray analysis using a 5% NaCl solution for 240 hours.

III. RESULTS AND DISCUSSION

A. Chemical Analysis:

The distinctive FTIR spectra of LA-MA Eutectic, MF-LA-MA microcapsules, MF-LA-MA/Alkyd, and MF-n-Tetra/Alkyd coat are shown in Fig. 2

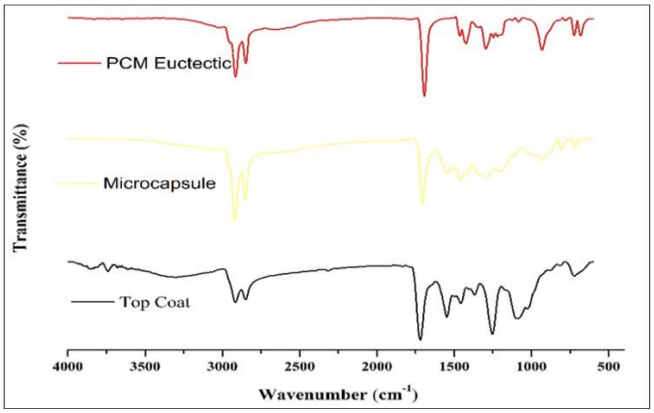

Fig 2 FTIR Spectra of LA-MA Eutectic PCM, LA-MA-MF Microcapsule, and MF-LA-MA Alkyd Coating Systems

B. Morphology:

Using POM and SEM, the morphological features of microcapsules was investigated.

➢ *Polarized Optical Microscopy:*

Using POM, morphological analysis of the created MF-encapsulated LA-MA Eutectic was performed. The optical micrographs of the dry and emulsified samples are depicted in the figures. The MF-encapsulated n-Tetra emulsion micrograph (**Fig.3**) demonstrates the presence of spherically shaped, uniformly distributed microcapsules with a smooth surface. It appears that no shells are broken during the mechanical stirring that is given to the emulsion during shell creation because there is no turbulence on the surface of the microcapsule. Between 2 and 20 m is the range of particle sizes that have been observed. The particle diameter increases following centrifugation and drying. The size increase has no impact on how the microcapsule grows into its final shape. The dried microcapsule sample is made up of tiny (2–20 μm), uniformly shaped particles.

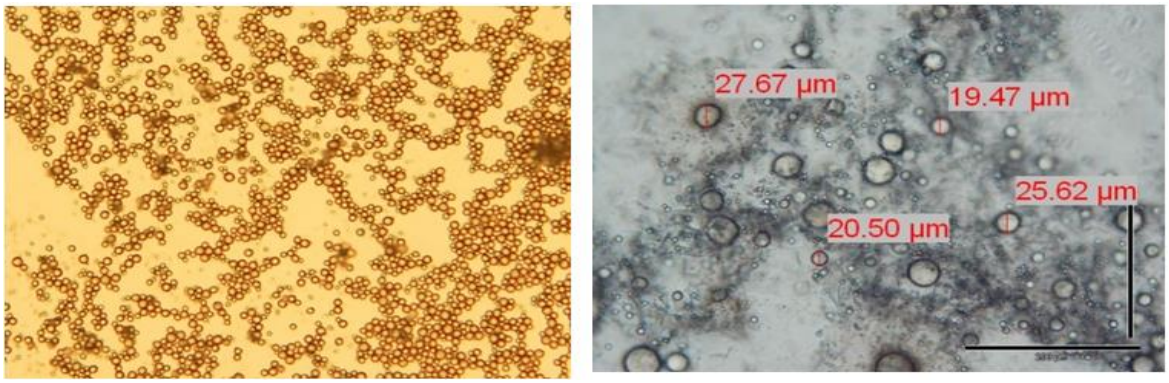

Fig 3 Polarized Optical Microscopic Images of LA-MA-MF Dried Microcapsules

➢ *Scanning Electron Microscopy*

The SEM images of the microencapsulated MF-LA-MA particles are shown in Figure. The core-shell microcapsules have what seems to be a compact, spherical shape. The dried microcapsules' SEM micrograph is shown in Fig. 4. The microcapsules' outer shells appear to be unharmed and unbroken by agitation during creation and subsequent processing. First figure depicts the shell surface at a higher magnification. The rough surface morphology seen is due to the deposition of colloidal particles on the surface of microcapsules, which results from the electrostatic attraction between the negatively charged colloidal particles and the positively charged MF pre-polymer particles.

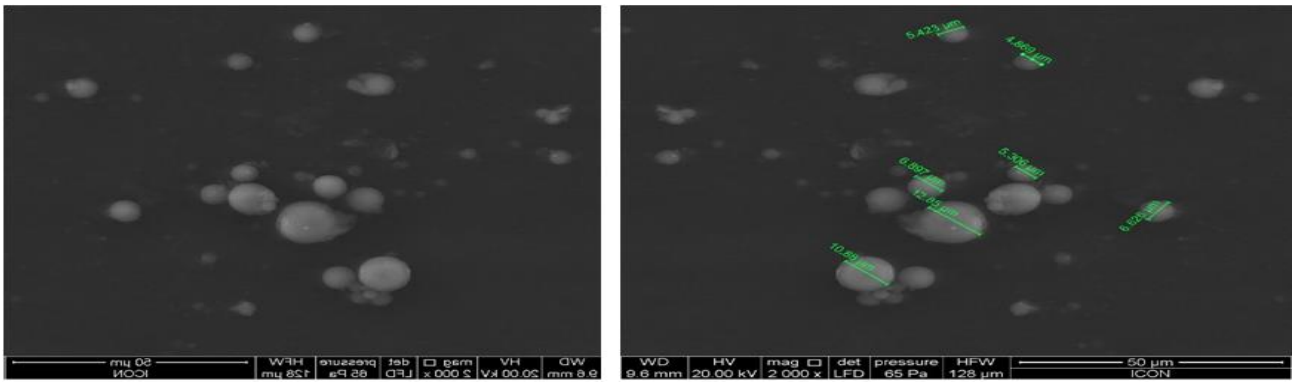

Fig 4 SEM Images of LA-MA-MF Microcapsules

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C. Thermal Energy Transfer Rate Apparatus:

We investigated the thermal energy transfer rate of alkyd enamel coated plates with and without microcapsules using our custom made heat storage transfer rate instrument. First, as indicated in Fig 5, the allocated slot was filled with the coated panels. It was set to 60°C and the heater was turned on. Using a painted panel as a barrier, the test's goal is to figure out how quickly heat moves from a heated chamber into an empty chamber. The LA-MA eutectic mixture's available enthalpy of melting rises as the microcapsule loading is changed between 3%, 6%, 9%, 12%, and 15%, resulting in a greater capacity for thermal energy storage.

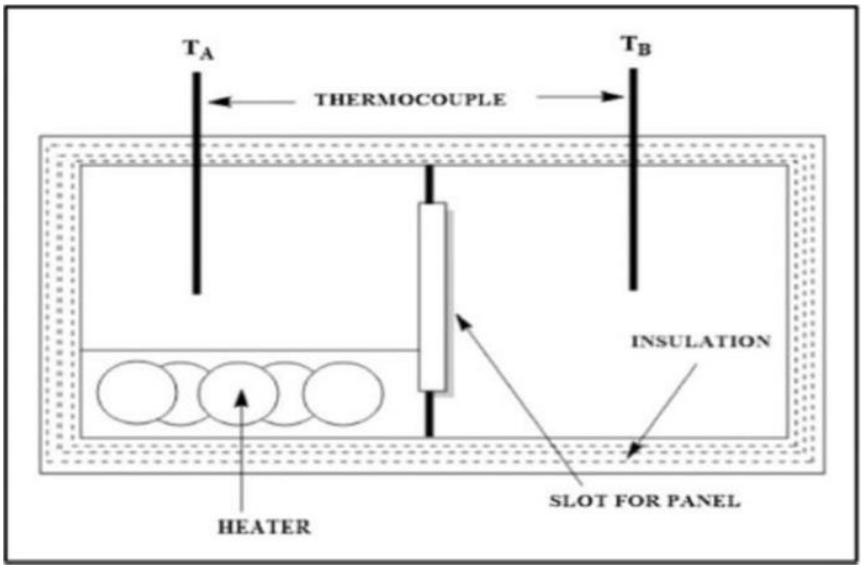

Fig 5 Hot Box Instrument

D. Thermal Properties:

The thermal parameters of the LA-MA eutectic, LA-MA-MF, and LA-MA-MF Alkyd systems were ascertained using DSC analysis and are depicted in Figs. 6 and 7. The encapsulation ratio and thermal energy storage capacity per unit mass affect LA-MA eutectic's PCM efficiency according to equation 1, the LA-MA eutectic in MF has an observed encapsulation ratio of 68.36% and an encapsulation efficiency of 68.38%. It has been found that the melting peaks temperatures of the LA-MA eutectic and the MF-encapsulated LA-MA-MF microcapsule are 33.01°C and 31.41 °C, respectively, lower than those of the LA-MA eutectic. This is because there is less heat movement through the shell and shell + coating than there is with pure LA-MA eutectic. LA-MA eutectic. LA-MA-MF Microcapsules and LA-MA-MF Alkyd coat crystallization temperature are 33.01^0C and 31.41^0C respectively.

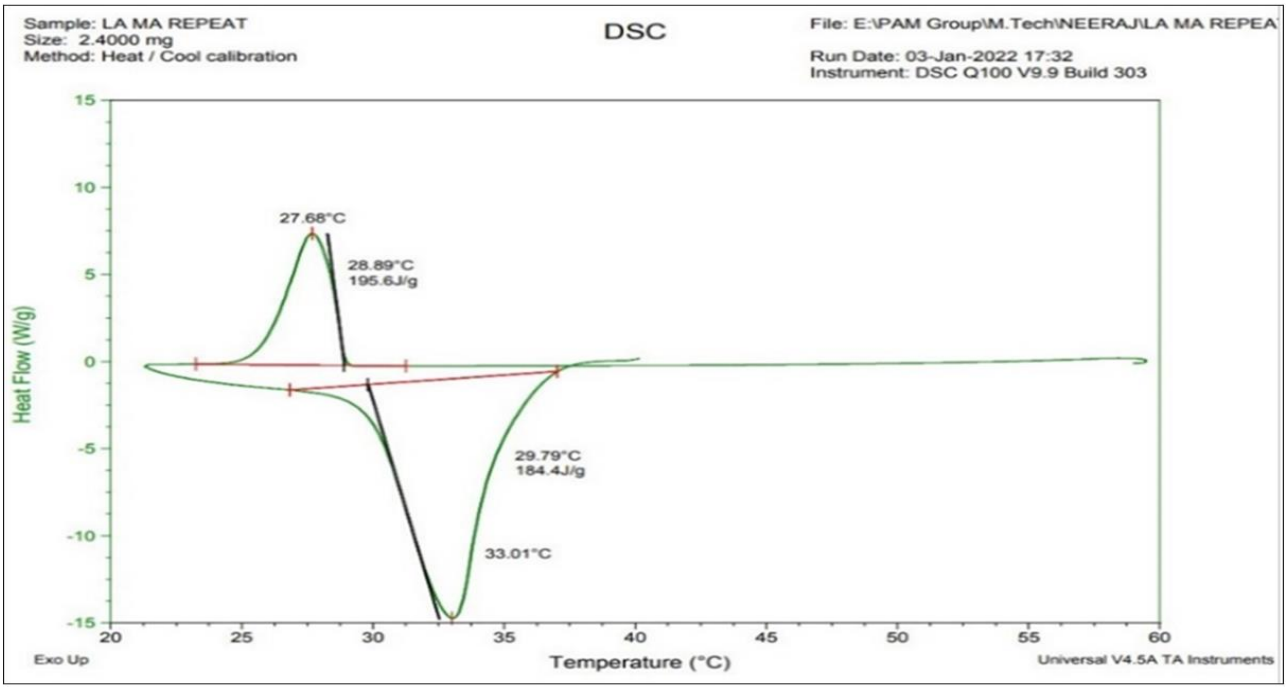

Fig 6 DSC Curve for LA-MA Eutectic Mixture

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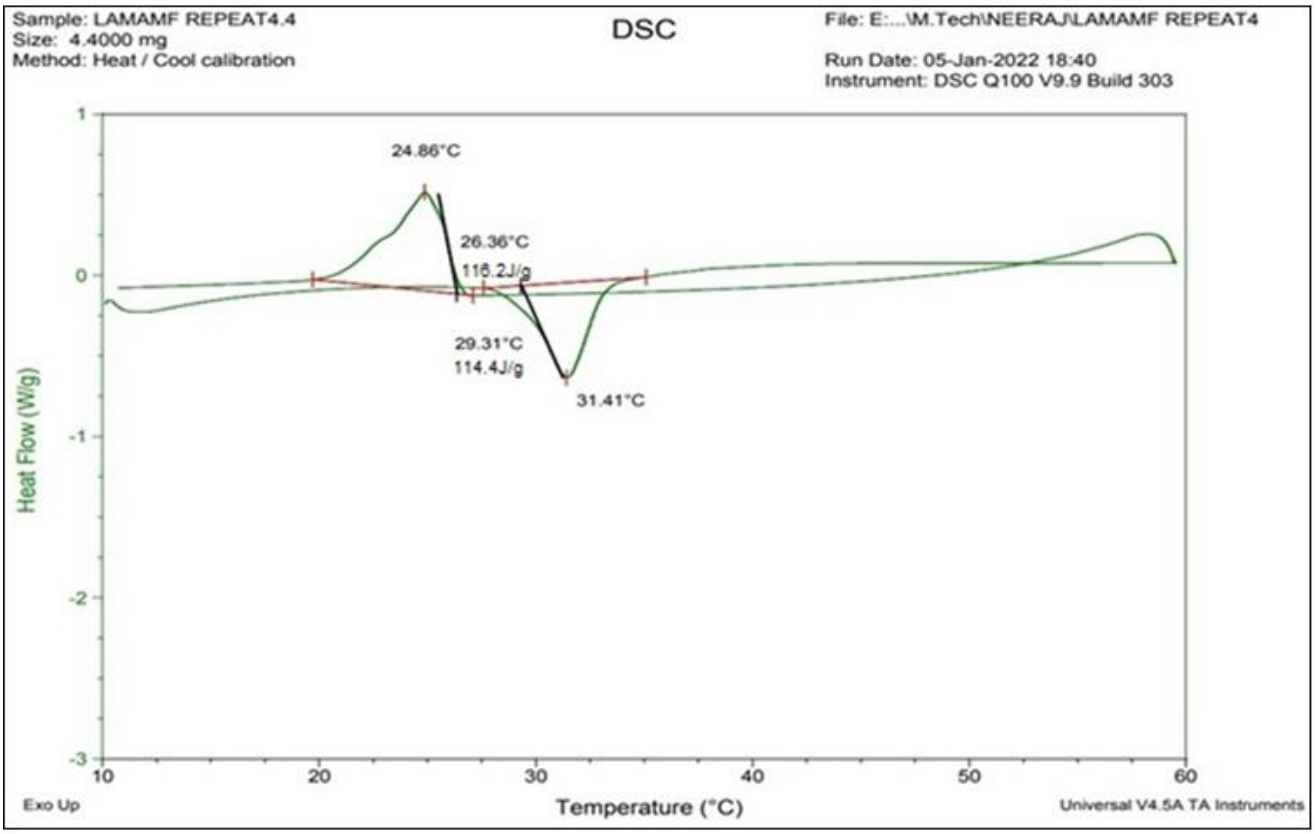

Fig 7 DSC Curve for LA-MA-MF Microcapsules

E. Thermal Stability of Microcapsule:

In **Fig. 8**, TGA curves for LA-MA-MF, MF shell, and LA-MA-Eutectic are displayed. As the temperature rises, it is seen that degradation causes the weights of the LA-MA Eutectic, MF, and LA-MA-MF to drop. The LA-MA Eutectic is observed to have a one-step degradation process with a start degradation temperature of 162^0C. By about 260^0C, the weight loss is finished. However, LA-MA-MF and LA-MA-MF coat demonstrate a two-step degradation process and exhibit better heat stability. The first weight deficit in LA-MA-MF is caused by the sample's remaining moisture. Because MF and alkyd improve the thermal stability of microencapsulated LA-MA eutectic, the computed weight loss rates for LA-MA-MF and LA-MA-MF alkyd coating are lower than those for LA-MA eutectic. Degradation of the LA-MA-MF and LA-MA-MF alkyd coats begins at 210^0C and 230^0C, respectively. At temperatures 350^0C and 354^0C, LA-MA-MF and LA-MA-MF alkyd showed signs of second phase deterioration.

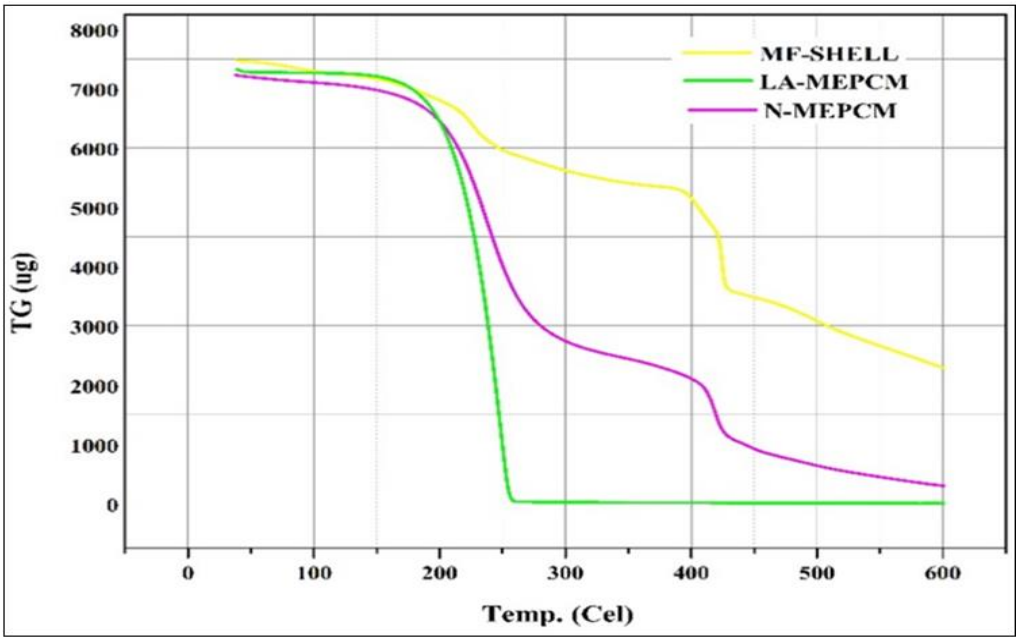

Fig 8 TGA Analysis of MF Shell, LA-MA MEPCM

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F. Salt Spray Study:

In **Fig. 9**, the applied panels are shown both earlier and after salt spray analysis. By checking for rust seeping from under the scratch marks, the amount of corrosion on the panels beneath the coating layer was measured. The panels will be subjected to a salt spray examination in order to evaluate their corrosion resistance. Every 24 hours, the coated panels underwent a corrosion resistance test. The outcomes of the salt spray analysis performed over 0-240 h are shown in Fig. 10. Knowing how the LA-MA-MF microcapsules affect corrosion resistance is necessary before they are integrated into the coating system. Given that corrosion is an electrochemical process, temperature is one of several elements that affect how quickly it occurs. After 170 hours, corrosion appears to start at the cut area of the panel for all systems. Even 240 hours of exposure to salt spray on all systems show that corrosion does not spread past the cut zone of the panel. Furthermore, it has been found that microcapsule loading boosts corrosion resistance. Additionally, it has been found that while there is a discernible difference in the degree of corrosion for coatings loaded with 0%, 3%, and 6% microcapsules, the degree of corrosion does not vary much for coatings loaded with 9%, 12%, and 15% microcapsules.

Fig 9 SST Unexposed and Exposed Panels (0%, 3%, 6%, 9%, 12% and 15% MEPCM Loading) (Left to Right)

G. General Coating Properties:

The test results of coated panels with different microcapsule weight percentages are shown in the table. According to the test results, pencil hardness declines as microcapsule loading increases. This might be caused by the coating's coating becoming less compact. The majority of the resin was sticking to the solid as the solid's content increased, which contributes to the matrix's low crosslinking density. The results show that as the ratio of LA-MA-MF microcapsule in the Alkyd enamel system increases, flexibility gradually decreases. It has been observed that mild breaking at bend occurs when the microcapsule loading exceeds 10% due to coating brittleness. The crosslinking of the system affects the coating's hardness and scratch resistance. Better crosslinking of the coating demonstrates extra compact structure, which in turn increases scratch resistance and hardness. The introduction of a higher weight percentage of a microcapsule in the system enhances the stiffness of the coating at a certain crosslink density, degrading the coating's scratch resistance and pencil hardness.

Table 2 General Coating Properties of Different Loading of the Microcapsule.

LA-MA-MF loading in Alkyd Enamel (wt%)	Flexibility	Scratch resistance (kg)	Pencil hardness
0	5	1	H
3	5	1	F
6	4	0.8	F
9	4	0.8	HB
12	3	0.5	HB
15	3	0.5	B

Key: 1, Absolute film lift-off at the bend; 2, Absolute breaking with at bend; 3, minor breaking at the bend; 4, discoloration at the bend; 5, not affected with the bend

IV. CONCLUSION

By using an in-situ polymerization technique using melamine formaldehyde as the shell material and a lauric acid-myristic acid phase eutectic mixture as the core material, encapsulation was accomplished satisfactorily. Several characterisation techniques supported the microcapsules' formation. The smooth and spherical surface of microcapsules is confirmed by SEM and POM. The presence of all core and shell material linkages is confirmed by FTIR analysis, which suggests that microcapsules formed without core and shell material reaction. The DSC results demonstrate the good encapsulation efficiency. In comparison to pure LA-MA eutectic, TGA study revealed improved heat stability for both microcapsules and microcapsule-incorporated coating. Increased microcapsule loading leads to a decline in coating characteristics (such as pencil hardness, flexibility, and scratch resistance). Compared to coatings without microcapsules, the corrosion resistance of coatings loaded with them is not significantly different. Gloss, water resistance, alkali resistance, and stain resistance were all tested for in paint qualities. The thermal performance of the coating was shown to improve with higher microcapsule concentrations. This demonstrates that the LA-MA-MF microcapsule with the enamel coating technology has a promising cool coating application.

- *Declaration of Competing Interest*

The author declared that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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