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An exploratory Study on the Preparation of a Silk Fibroin-Chitosan Based Organic Solid-Liquid Transition Type Phase Change Materials (PCMs): Microcapsule and Foam Structures

Zulal Gunay [1] 0000-0003-3893-9876
Ceren Nair [2] 0000-0001-9063-6325
Oguz Bayraktar [3] 0000-0003-4210-2825

[1,2,3] Ege University / Engineering Faculty / Department of Bioengineering, 35100, Bornova, İzmir, Türkiye

ABSTRACT

Phase change materials (PCMs) can store and release latent heat by making phase transitions between solid-solid or liquid-solid phases at specific temperature ranges. In the preparation of silk fibroin (SF) and chitosan (CHI) based phase change microcapsules and foam structures, the usage of virgin coconut oil (VCO) as phase change agent was investigated, both forms were successfully prepared and characterized. Scanning Electron Microscope (SEM) and optical microscope with heating block analyzes were performed on microcapsules. SEM, Fourier-transform infrared spectroscopy, and differential scanning calorimeter analyzes were performed on foams. SF and CHI-based microcapsules had homogeneous size distribution and were thermally stable up to 60 °C. Characteristic properties of the foam structures changed with the amounts of SF and CHI, and phase change occur at around 25 °C, the melting temperature of VCO, resulting in energy absorption of 21.98 J/g. Microcapsule and foam PCMs obtained can be used in different medical and thermoregulated textile applications.

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Silk fibroin, chitosan, phase change materials, foam, microcapsule

1. INTRODUCTION

Phase change materials (PCMs) are compounds that, when melted and solidified at specific temperatures, may store or release huge amounts of energy. Many phase change materials melt and solidify at a wide range of temperatures, making them appealing for a variety of applications such as solar and nuclear heat storage, packed bed heat exchangers, and thermoregulated textiles [1]. PCMs offer different advantages due to their various melting and solidification temperatures. With the development of this technology, PCMs have been used for conditioning of buildings, cooling of electric and heat engines, food and beverage industry, cooling of greenhouses, waste heat recovery, heating and cooling of water, solar energy units, production of textile materials for human comfort and medical applications [2]. In medical fields, PCMs can be used to keep vaccines in the correct temperature range (2-8 °C), transport blood and various temperature sensitive products [2]. In a different study conducted in 2009, a PCM-based heat application system was used in the treatment of Buruli ulcer [3]. PCMs are also actively used in gel pads and orthopedic products.

In thermoregulated textiles or heat storage textiles, PCMs with a phase change temperature range just above and just below human skin temperature is being employed. When the surrounding temperature is higher than their phase change temperature, these textiles accumulate heat from the environment, and when the temperature is lower than that value, they release heat [4]. Because paraffin waxes or linear chain hydrocarbons have large heat storage capabilities and their phase transition temperatures are within the range of human comfort temperature, paraffin

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waxes or linear chain hydrocarbons are favored for thermoregulated textiles [4].

PCMs can be prepared using numerous encapsulation techniques including in situ polymerization, interfacial polycondensation, suspension polymerization, complex coacervation, and freeze-drying to encapsulate PCMs in the form of microcapsules [4] or foam structures [5]. PCMs can be divided into two classes, organic and inorganic. Inorganic PCMs such as salt hydrates, salts, metals, and alloys can provide volumetric thermal energy storage capacity approximately twice that of organic PCMs [6]. However, inconsistent melting, corrosive nature, and subcooling effects limit the applications of inorganic PCMs in many areas. Being environmentally friendly, reusable, non-toxic, and abundant in nature, natural PCMs increase their usage areas and decrease their energy requirements.

Chitosan and silk fibroin are both naturally occurring materials. Chitosan is a polysaccharide made by the N-deacetylation of chitin from crab or shrimp shells. It has biocompatibility, biodegradability, nontoxicity, physiological inertness, antimicrobial characteristics, heavy metal ions chelation, gel-forming properties, and hydrophilicity, as well as a remarkable affinity for proteins [7]. Chitosan enables the preparation of gel and sponge materials thanks to its 3-dimensional scaffold, and the preparation of films and fibers thanks to its 2-dimensional scaffold. These created materials have beneficial effects on wound healing [8].

Bombyx mori silkworm larvae create silk-fibroin, a fibrillar protein. It is biocompatible and biodegradable, with great tensile strength and elasticity [9,10]. Chitosan and silk fibroin are biopolymers that are ideal for encapsulating bioactive natural compounds due to their unique characteristics [11,12]. It is stated in the literature that silk fibroin is used effectively in the PCM structure and is suitable for nonionic, ionic, and mixed surfactants applications [13]. It has been observed in different studies that silk fibroin and chitosan work in harmony as a phase change material [14, 15].

Fatty acids and their derivatives are PCM agents that has many superior properties such as suitable melting temperature range, high heat capacity, full melting, small volume change, low vapor pressure, non-toxic, low cost, non-flammable, non-corrosive for metal containers and good thermal stability. Phase change temperature and latent heat are two basic parameters of phase change materials (PCM). The phase transition temperature and latent heat of saturated fatty acids increase with carbon chain length. Also, the application of fatty acid as PCM is affected by other physical and thermal properties of fatty acids, such as density, specific heat, and thermal conductivity [16]. Although there are different studies on the use of edible organic acids as a phase change agent, it has been stated that the use of virgin coconut oil (VCO) is active and effective [15, 17, 18]. As a fatty acid, VCO is considered as a good PCM that has a melting point approximately at 24 °C, also thermally stable under 200 melt-freeze cycles almost at room temperature heat capacity range [19]. In recent years, the use of fatty alcohols as thermal energy storage material has been attracted a great deal of interest because of their low cost than paraffin waxes and having high heat density and a wide range of melting temperatures [20]. When the VCO properties were examined, it was seen that the melting point changed between 22-24 °C, the heat of fusion was 103.25 kJ/kg, and the density was 91.36 kg/m^3. The phase change of this component is in the comfort temperature range of 24-27 °C [21]. VCO can be actively used in the production of PCMs with the advantages of low cost, high boiling point, fast freezing, and non-reactive natural material.

The use of PCMs has increased, especially in the last 20 years, and different studies have been carried out on this subject. Most of the studies are on encapsulation of PCMs, increasing encapsulation efficiency, and improving heat storage properties. The choice of encapsulation method depends on the properties of the material to be used as PCM and the area of use [22].

There are different applications in the literature where VCO is used as an agent. Saleel et al. 2019, used PCM with VCO on vehicle roofs to prevent hypothermia in vehicles, and they observed that the interior temperature of the vehicle could be reduced by an average of 15 °C as a result of the trials [23]. As a result of the study they carried out in 2017, Irsyad and Harmen revealed that PCMs containing VCO in foam structure with high thermal conductivity can play an effective role in reducing the room temperature. It has been observed that heat transfer via forced convection on the container surface can reduce the ambient temperature by 0.82-1.29 °C with 1-1.5 m/s air velocity and 30-33 °C air temperature [24]. Organic PCMs produced in the form of microencapsules using VCO can be used for thermoregulation applications by integrating them into cellulosic fibers [25]. In their study, Saraç et al. (2019) produced VCO-based microcapsule PCM and applied the capsules they produced to cellulosic-based (denim and cotton) fabrics. Microencapsulated PCMs and processed fabric samples were characterized using Fourier transform infrared spectroscopy, differential scanning calorimetry, thermal gravimetric analysis, and scanning electron microscopy, resulting in the fabrics having remarkable latent heats between 6.7 and 14.9 J/g. demonstrated that it can be effective at peak melting temperatures of 21.5 °C and 22.1 °C with microencapsulated PCMs. [25]

In our previous work [4] PCM (n-eicosane) containing microcapsules were prepared by complex coacervation of silk fibroin (SF) and chitosan (CHI) and examined for their chemical characteristics, melting and crystallization properties of the microcapsules by utilizing FT-IR, DSC, and TGA.

In this study; we use organic materials such as silk fibroin, virgin coconut oil and chitosan which don't contain allergic hazards. In this experiment; VCO was used as a PCM agent, and PCM was studied as SF-CHI-based microcapsule and foam structure, the prepared PCM microcapsules with VCO as phase change material were subjected to heating from room temperature to 60 °C and 70 °C and cooling back to room temperature again to determine thermal stabilities of PCM microcapsules using heating block-microscope experiments. In our previous study [5] a highly biodegradable PCM (coconut oil) containing foam structure was prepared with silk fibroin and chitosan as biopolymers. In this study further characterization of this foam material encapsulating PCM (VCO) was performed.

2. MATERIAL AND METHOD

2.1 Material

For the preparation of the PCM microcapsules PCM (VCO) with a purity of over 98%, emulsifier Span-20 (Fluka in Singapore) and Low molecular weight chitosan (R-Aldrich Chemicals) with a deacetylation degree of 75-85% and a viscosity of up to 200 cps were used. Silk fibers were provided by Koza Birlik (Bursa, Turkey). Acetic acid (Merck, Germany) was utilized to dissolve the chitosan. The crosslinking of microcapsule walls was done with glutaraldehyde (50% water solution) purchased from Fluka, Switzerland. Virgin coconut oil (VCO) used in the microcapsule and foam structures was purchased from the local grocery store.

2.2 Degumming of Raw Silk

Raw silk was treated in the aqueous 0.5% sodium carbonate solution for 90 minutes at a solid-liquid ratio of 1:30. This step was repeated at least 3 times. Degummed silk was washed with deionized water for 5 minutes. After treatment, degummed silk was left to dry at 40 °C for 17 hours in the oven. The weight loss after the degumming process was 25% due to the removal of sericin from the silk fibroin fibers

2.3 Preparation of Silk Fibroin & Chitosan Solutions

Silk fibroin solution was prepared using the Ajisawa method. First, degummed silk fiber was dissolved in a mixed triad solvent of $CaCl_2.2H_2O$ / H_2O / EtOH with a 1:8:2 molar ratio at 78 °C and 125 rpm stirring speed for about 2 h. Then, the solution was dialyzed using cellulose tubular membranes (20 cm length Snakeskin, MWCO=10.000) in distilled water for a minimum of three days at 4 ºC. Deionized water was changed 6 times in three days.

The %1 chitosan solution was prepared with 2% aqueous acetic acid solution. The solution was stirred at 700 rpm for 20 hours at a magnetic stirrer.

2.4 Preparation of SF-CHI microcapsules containing PCM

Phase change material (VCO) incorporated silk fibroin-chitosan microcapsules were manufactured through the complex coacervation of silk fibroin and chitosan, described in our previous study [4]. As seen in Figure 1 silk fibroin solution and PCM were mixed to obtain emulsion phase then chitosan solution was added at a final pH of 3. Then pH was adjusted to 5.1 to initiate the coacervation around the emulsions at 40 ºC.

2.5 Preparation of Silk Fibroin-Chitosan Foam Material Containing PCM

Silk fibroin, chitosan, and virgin coconut oil were mixed at different ratios (e.g, **S4**: 20% SF, 40% CHT, 40% VCO; **S5**: 20% SF, 60% CHT, 20% VCO; **S6**: 40% SF, 20% CHT, 40% VCO; **S7**: 60% SF, 20% CHT, 20%). After mixing different ratios, solutions were well stirred with UltraTurrax for 5 minutes. Stirred solutions were then frozen at 4 °C for 24 hours. Frozen solutions were then freeze-dried for 3 days in a freeze dryer.

2.6 Characterization of Prepared Materials Containing PCMs

Microcapsules containing PCMs were investigated by optical microscopy equipped with a heating block and a camera to visualize the thermal stability of microcapsules at temperatures between 24 and 70 ºC. Morphological analyses of prepared microcapsules and foam materials were carried out using scanning electron microscopy (SEM). The surface functional groups of the PCMs were analyzed by an FT-IR (Digilab FTS 3000 Mx) with a scanning number of 50 and a resolution of 4 cm^{-1}.

3. RESULTS AND DISCUSSION

SEM analysis was performed to observe the morphological features of the microcapsules. Their thermal stabilities were investigated by heating microcapsules from room temperature to the first 70 and then 60 ºC in the heating block. In foam structures, the morphology of the structures was determined by SEM analysis, and the heat release and structural properties were determined by DSC and FT-IR analyses, respectively.

3.1 Morphology of Microcapsule PCM

The results of our SEM analyzes are presented in Figure1a-c below. When the SEM images of the microcapsule PCM samples in Figure 2 are examined at 500x and 3500x magnification, it is seen that the sizes of microcapsules ranged approximately between 5 to 50 µm. The observed microcapsules were spherical in shape. The average mean diameter was found to be approximately 35 µm and distributed homogeneously. The outer surfaces of microcapsules were wrinkled (Figure 2a) possibly due to the presence of silk fibroin with a fibrous structure.

3.2 Thermal Behavior of Microcapsule PCM

Figure 3 shows the optical microscope photographs of microcapsule PCM samples subjected to heating from room temperature to 70 °C and cooling them back to room temperature on a heating block. It was observed that the PCM microcapsule structure irreversibly degraded at temperatures exceeding 60 °C. Heating from room temperature to 70 °C, after 60 °C the wall material of the microcapsule structure loses its integrity and PCM (VCO) is released to the outer environment (Figure 3 c,d).

Figure 4 shows the photos of the PCM microcapsule samples being heated to 60 °C starting from 23.1 °C and then cooled to 29 °C (top photos shown from left to right (Figure 4a-d) were taken at increasing temperature during the heating phase, the bottom photos shown from right to left (Figure 4e-h) were taken at decreasing temperature during the cooling phase). As seen in the photographs, there is no deterioration in the structure during the heating process up to 60 °C. Due to the evaporation of water during the heating process, the photographs in the cooling phase were blurred, but no deterioration in the microcapsule structure and release of PCM (VCO) from microcapsules were observed. This result revealed that the prepared microcapsule PCM was thermally stable up to 60 ºC.

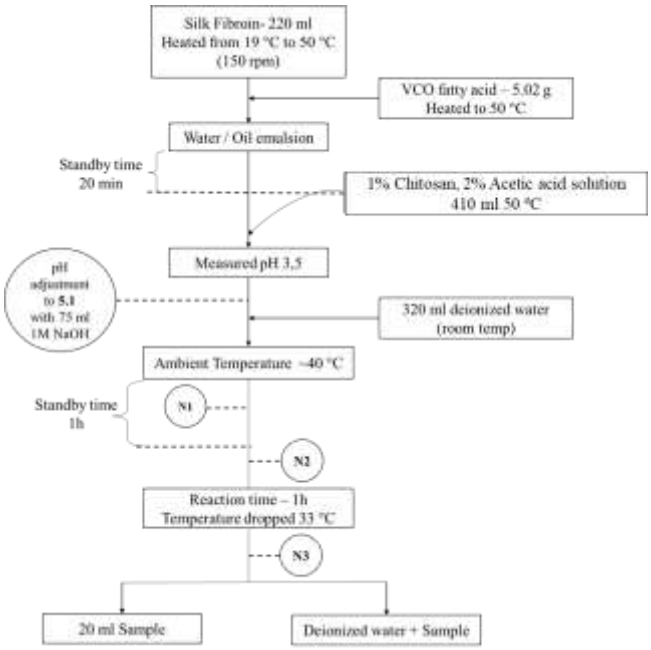


Figure 1. Procedure for the preparation of SF-CHI based PCM microcapsules

Figure 2. SEM micrograph of the microcapsules containing PCM, at different magnifications a: 500x, b and c: 3500x

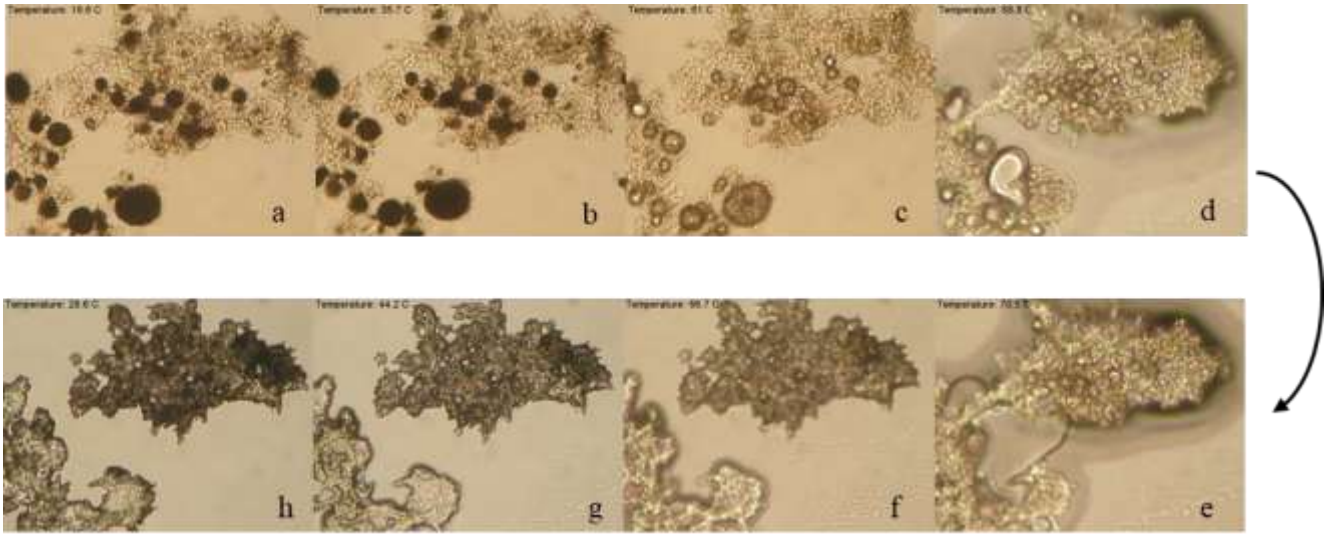


Figure 3. Optical visualization of microcapsule PCMs on heating block heating from room temperature to 70 ºC and cooling back to room temperature. a) 19.5 °C, b) 35.7 °C, c) 61 °C, d) 68 °C, e) 70.5 °C, f) 66.7 °C, g) 44.2 °C, h) 28.6 °C

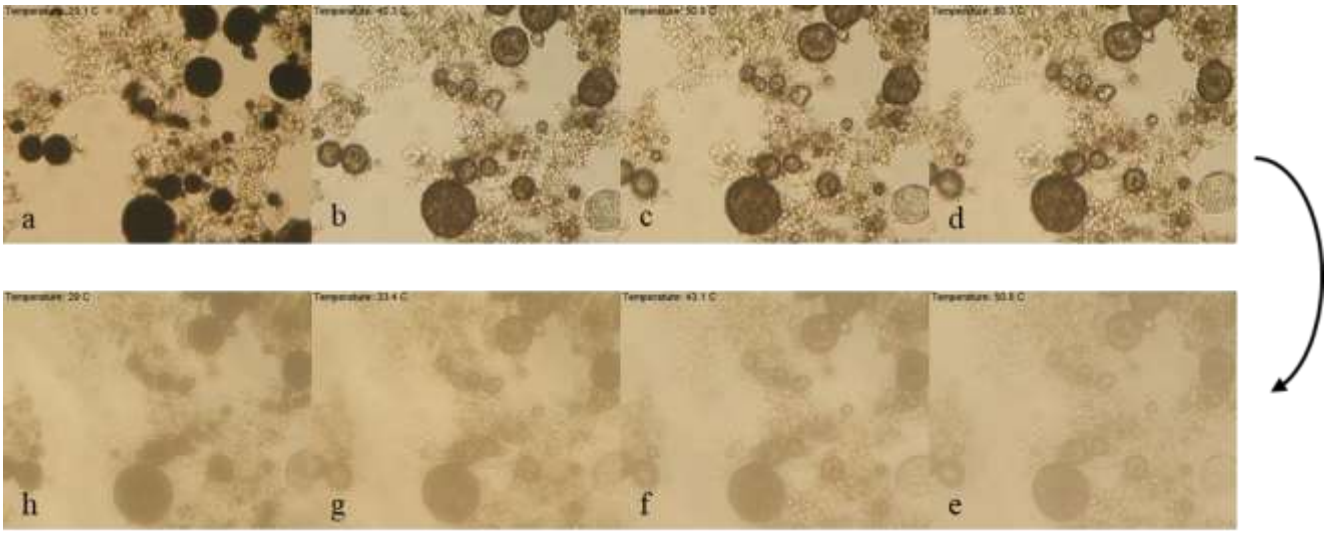


Figure 4. Optical visualization of microcapsule PCMs on heating block heating from room temperature to 60 ºC and cooling back to room temperature. a) 23.1 ºC, b) 40.3 ºC, c) 50.8 ºC, d) 60.3 ºC, e) 50.8 ºC, f) 43.1 ºC, g) 33.4 ºC, h) 29 ºC.

3.3 Morphology of Foam PCM

In Figure 5, SEM images of the PCM foam material samples obtained with a mixture of silk fibroin and chitosan are shown. In these images, the magnification was at 2500x. As seen in these images, there are homogeneously distributed small-sized pores in cross-section. The average value of pore diameters was found to differ as the component ratio in the samples changed. It is observed that as the chitosan ratio increased, the porosity of samples was decreasing. Also, pore sizes were found to be higher with the samples that consisted of higher ratios of SF. The relatively high surface area due to the homogeneously distributed smaller size pores in the structure is desirable in terms of high-performing PCM.

3.3 FT-IR Analysis of Foam PCM

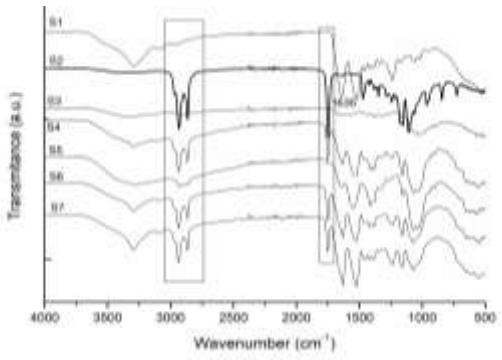
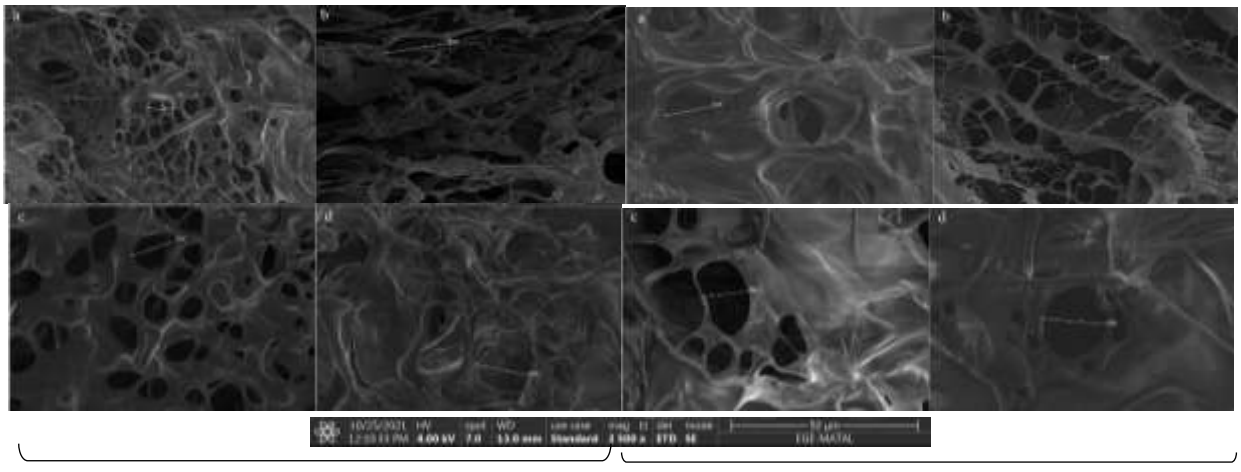


Figure 6. FT-IR spectra of foam samples S1) Pure Silk Fibroin Foam, S2) Virgin Coconut Oil (VCO), S3) Chitosan Powder, S4) 20% SF, 40% CHT, 40% VCO, S5) 20% SF, 60% CHT, 20% VCO, S6) 40% SF, 20% CHT, 40% VCO, S7) 60% SF, 20% CHT, 20% VCO [5].



Cross-section SEM micrographs | Surface SEM micrographs

Figure 5. SEM micrographs of 4 samples at 2500x magnification (Cross-section (left-hand side) and surface (right-hand side). Sample compositions : **a)** 20% Silk fibroin, 40 % Chitosan, 40% Virgin Coconut Oil; **b)** 20% Silk fibroin, 60% Chitosan, 20% Virgin Coconut Oil; **c)** 40% Silk fibroin, 20% Chitosan, 40% Virgin Coconut Oil; **d)** 60% Silk fibroin, 20% Chitosan, 20% Virgin Coconut Oil.

For the identification of foam material composition (chemical composition and organic compounds), the most widely used analytical tool is FT-IR. FT-IR spectra of coconut oil, silk fibroin, chitosan, SF/CHI foam material containing coconut oil in the range of 4000-400 cm^{-1} were recorded and presented in Figure 6. Characteristic absorption peaks of silk fibroin, virgin coconut oil, and chitosan were observed.

FT-IR spectrum of chitosan exhibited characteristic absorption bands. The absorption band at 1080 cm^{-1} refers to the skeletal vibrations involving the CO stretching, at 3448 cm^{-1} corresponds to the hydroxyl group which is characteristic of chitosan saccharide structure [18, 19]. At wavenumber 1653 cm^{-1} bands correspond to C=O stretching in amide group [26, 27], at wavenumber 1560 cm^{-1} bands correspond to N-H bending in the amide group [26] at wavenumber 1595 cm^{-1} bands corresponds to N-H bending in nonacetylated 2-amino glucose primary amine [4, 28].

Silk I and II are well-known major silk fibroin structures [4, 29]. Silk I is a metastable conformation composed of random coils and a-helix structures. Silk II is primarily composed of antiparallel β-sheets. FT-IR Spectrum of SF-based foam structure confirmed the β-sheet conformation showing typical amide absorption bands at 1636 cm^{-1} (Amide I), 1526 cm^{-1} (Amide II), and 1231 cm^{-1} (Amide III).

The conformational changes of fibroin (Silk I structure) owing to foam material creation with chitosan were revealed using the FT-IR spectrum of silk fibroin foam (indicating Silk II structure). When compared to the β-sheet dominant conformation of control SF foam, the development of prominent peaks of SF-CHI foam materials at 1231 cm^{-1} indicated that the dominant conformation was silk II. Hydrogen bonding and electrostatic interactions between SF and CHI molecules may be responsible for the presence of β-sheets (Silk II). The development of a signal at 3294 cm^{-1} revealed an intermolecular hydrogen bond. Blending or complexing with another biopolymer, as well as the freeze-drying process, led the secondary structure of the SF molecule to transition from Silk I to Silk II. Our findings are consistent with those published in the literature for similar systems [30-32]. CHI is responsible for the peak (1062 cm^{-1}) linked with aliphatic amino groups. Visual inspection of the FT-IR spectrum shows that absorption bands at wavenumbers 2954 cm^{-1} stretching –C-H [CH_3], 2921 cm^{-1} asymmetric stretching –C-H [–CH_2], 2853 cm^{-1} symmetric stretching –C-H [–CH_2], 1743 cm^{-1} stretching – C = O, 1463 cm^{-1} [Bending –C–H [CH_2], 1417 cm^{-1} Bending =C–H, 1377 cm^{-1} symmetrical bending –C–H [CH_3], 1232 cm^{-1} stretching –C–O, 1158 cm-1 stretching – C–O, 1116 cm-1 stretching –C–O, 963 cm^{-1} trans olefin bending –HC=CH–, 870 cm^{-1} bending =CH_2 (wagging) and 721 cm^{-1} bending –(CH_2)n– (rocking) for coconut oil sample [33].

The aliphatic C-H stretching vibration and the in-plane rocking vibration of the CH_2 group were attributed to the absorption peaks at 1472 and 721 cm^{-1} in the spectra of coconut oil and SF/CHI foam material containing coconut oil, respectively.

3.3 DSC Analysis of Foam PCM

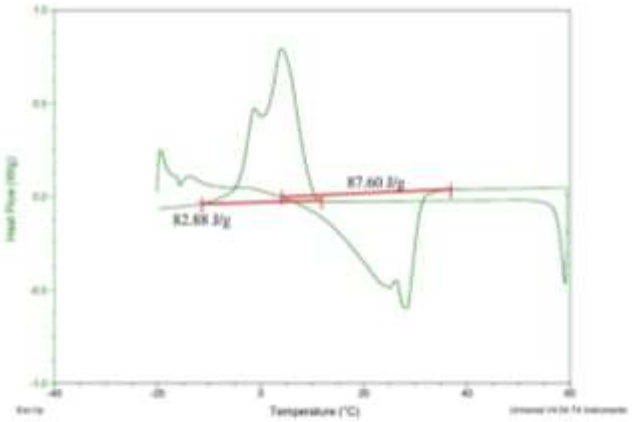


Figure 7. DSC thermograms of Virgin Coconut Oil (VCO)

In Figure 7, VCO thermograms revealed endothermic and exothermic peaks. It was observed that VCO has a freezing point that causes VCO to solidify at almost 4.11 °C. This exothermic peak had an energy release of 82.88 J/g. An endothermic peak at approximately 25°C was observed corresponding to energy absorption of 87.60 J/g. The results of previous studies [19], revealed that virgin coconut oil had a melting temperature of 24.0 ± 1.5 °C with a solidifying temperature of 22.5 °C. As seen in Figure 7 the thermograms that showed endothermic and exothermic peaks were similar to the results reported earlier in the literature [19]. The latent heat of melting of VCO was reported as 93.00 ± 9 J/g. Our values agree well with most literature values of latent heat of melting determined by DSC in other studies.

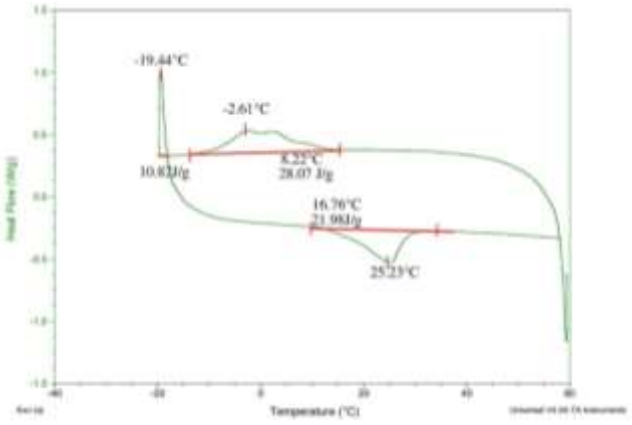


Figure 8. DSC thermograms of Sample 6 (S6) which contains 40% SF, 20% CHT, 40% VCO as Phase Change Material (PCM)

As shown in Figure 8, the foam sample had a similar thermogram curve to the VCO. As the thermogram curve

shows, the foam PCM had an exothermic peak at almost 4 °C by releasing the energy of 28.07 J/g. Similar to the original VCO thermogram, foam PCM had an endothermic peak at almost 25 °C that resulted in energy absorption of 21.98 J/g. In the preparation of foam PCMs, VCO was added such that 40% of the total weight of the foam PCM consists of VCO. VCO content of foam PCM was determined as 35 % by weight using the latent heat of melting and freezing of VCO.

4. CONCLUSION

In this study, microcapsule and foam forms of PCM were successfully prepared using two different preparation techniques. The PCM microcapsules with virgin coconut oil were successfully prepared by complex coacervation of silk fibroin and chitosan . The thermal behavior of the prepared PCM microcapsules between room temperature and 60 ºC was determined and observed using a microscope equipped with a heating block. The prepared microcapsule PCM was thermally stable up to 60 ºC. In this study, SF-CHI foam materials including 40% virgin coconut oil with homogeneously distributed small-sized pores based on the SEM analysis has been prepared for the first time. Characteristic properties of the foam structures changed with the amounts of SF and CHI, and phase change occur at around 25 °C, the melting temperature of VCO, resulting in energy absorption of 21.98 J/g. Both microcapsule and foam PCMs can potentially be used alone or together for different, specifically for biomedical applications in thermoregulated non-toxic and biodegradable products.

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