(REFEREED RESEARCH)

FABRICATION OF MICROENCAPSULATED PCMs WITH NANOCLAY DOPED CHITOSAN SHELL AND THEIR APPLICATION TO COTTON FABRIC

NANOKİL KATKILI KİTOSAN DUVARLI MİKROKAPSÜLLENMİŞ FDM ÜRETİMİ VE PAMUKLU KUMAŞA UYGULAMASI

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ABSTRACT

In this study, preparation of composite microcapsules with clay nano particles (CNPs) doped chitosan shell and paraffin core was carried out by oil-in-water (o/w) complex coacervation method. It was aimed to microencapsulate phase change materials (PCMs) within composite shell material composed of organic and inorganic components. The effect of surface active materials having different hydrophilic/lipophilic balance (HLB) on preparation and properties of the microcapsules was also investigated. Thermal properties, morphology, chemical structure of the prepared microcapsules containing PCMs (MicroPCMs) were analyzed by differential scanning calorimeter (DSC), Thermogravimetric analysis (TGA), optical microcopy, and Fourier transform infrared (FT-IR) spectroscopy, respectively. The thermo-regulation effect of the MicroPCMs on the cotton fabric was investigated.

Keywords: PCM, chitosan, nanoclay, microcapsule, cotton fabric, T-history

ÖZET

Bu çalışmada, su içinde yağ kompleks koaservasyon metodu ile nano kil katkılı kitosan duvarlı, parafin çekirdekli kompozit mikrokapsül üretimi gerçekleştirilmiştir. Çalışmada, inorganik ve organik bileşenler ihtiva eden kompozit duvar içine faz değiştiren madde (FDM) mikrokapsüllenmesi amaçlanmıştır. Ayrıca farklı hidrofilik/lipofilik denge (HLB) değerine sahip yüzey aktif maddelerin mikrokapsül üretimine ve özelliklerine etkisi de araştırılmıştır. Üretilen mikrokapsüllerin (MikroFDM) ısıl özellikleri diferansiyel taramalı kalorimetre (DSC) ve termogravimetrik analiz (TGA), morfolojileri optik mikroskop, kimyasal yapıları FT-IR ile karakterize edilmiştir.

Anahtar Kelimeler: FDM, kitosan, nano kil, mikrokapsül, pamuk kumaş, T-history.

1. INTRODUCTION

PCMs can store and release large quantities of latent heat during a phase change process efficiently and repeatedly. The temperature of PCM remains constant during its phase change from liquid to solid and from solid to liquid. They have been used to regulate the surrounding temperature due to their high latent heat capacity and isothermal behavior. However, encapsulation of solid-liquid PCMs with proper shell material is required in order to control the volume changes of the core material during the period of the phase change. Microencapsulation also prevents PCMs from leakage when melted, isolates them from the influences of the external environment, and increases their thermal conductivity [1, 2]. The encapsulation of PCM as a core is the technique that holds PCM inside a polymer or an inorganic shell [3]. Microencapsulation processes are generally classified as chemical and physical ones. One of the chemical processes is complex coacervation which involves complex structure formation by the interaction of two oppositely charged colloids. In this method, core material is emulsified within a polymer solution adding a surface-active agent and complexation between the oppositely charged polymer colloids is carried out over a narrow pH range [4, 5]. Recently, there has been growing interest in encapsulation of paraffin-waxes as energy storage materials by complex coacervation method [6]. Hawlader et al. encapsulated a commercial type paraffin wax by using gelatin, gum Arabic and acacia solutions as shell materials. They evaluated the encapsulation ratio, hydrophilicity, energy storage capacity, and particle size distribution in the complex coacervation process and also

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indicated that prepared microcapsules preserved heat storage capacities constant even after 1000 thermal cycles [7, 8]. In their other study, Hawlader et al prepared encapsulated paraffin by complex coacervation as well as spray-drying method [9]. Rong et al. prepared thermally stable, uniform, and spherical microcapsules by complex coacervation of gelatin and a hydrolyzed co-polymer of styrene and maleic anhydride [10]. Özonur et al. (2007) encapsulated natural coco-fatty acid by complex coacervation and achieved microcapsules with size of 1mm. They concluded that gelatin+gum Arabic mixture was the best shell material for microencapsulation of coco fatty acid mixtures between the several alternative shell materials [11]. Önder et al. prepared microencapsulated *n*-hexadecane, *n*-octadecane and *n*-nonadecane by gum arabic–gelatin shell using complex coacervation method [6]. Bayés-García et al. fabricated phase change microcapsules with different shell compositions from two different coacervates: Sterilized Gelatine/Arabic Gum and Agar-Agar/Arabic Gum [12]. Deveci and Başal prepared microencapsulated n-eicosane by complex coacervation of silk fibroin and chitosan [13]. Li et al. microencapsulated n-octadecane in gelatin-gum Arabic shell, polyurethane shell and styrene-based copolymer shell via complex coacervation, interfacial polymerization and suspension polymerization, respectively [14]. In recent year, some attempts have been made to encapsulate paraffin with inorganic materials due to some limitations of polymeric shells, such as flammability and low heat conductivity [15-19]. In this study, microencapsulated PCMs (MicroPCMs) were prepared by using oil-in-water complex coacervation of chitosan and nano clay pair. Therefore, it was aimed to investigate the effect of organic and inorganic materials within a single molecular scale composite. It was focused on thermal properties such as heat releasing and storing temperature and enthalpy, thermal stability, morphology and chemical structure of the prepared microcapsules. It was also investigated the fabrication of thermo-regulating cotton fabric by applying the prepared microcapsules.

2. MATERIALS AND METHODS

2.1. Materials

Chitosan (CH, Mw of 100.000-300.000, Acros Organics) as polycation polymer and clay-nano particles (≤ 25 micron, CNPs, Sigma Aldrich, hydrophilic bentonite) as inorganic polyanion component were used as shell materials for microencapsulation of n-eicosane (Alfa Aesar). Glutaraldehyde (2.5 %, Sigma Aldrich) as cross-linker was used to improve the stability of the microcapsules. Chitosan polymer was dissolved in acetic acid (100%, Sigma Aldrich). Span 20, Span 80, Tween 20, Tween 40, Tween 80 as surfactant with 8.6, 4.3, 16.7, 15.6 and 15.0 HLB values, respectively, were used to emulsify core material within aqueous polymer solution.

The woven fabric scoured and bleached (100 % cotton) with the weight of 122 g/m^2 (57 yarns per cm in warp direction and 40 yarns per cm in weft direction) was used for microcapsule application. Perapret booster XLR (from BASF), Perapret PU new (from BASF) and Perrustol VNO (from Rudolf Duraner) were used as resin, catalyst and softener, respectively.

2.2. Preparation of microencapsulated PCMs

Complex coacervation takes places in the mixed polymer solution of two oppositely charged polymers [20]. In this study, microcapsules containing n-eicosane was prepared by complex coacervation of chitosan polymer as polycation and CNPs as anion component. In the process, CNPs (0.6 gram or 1.2 gram) and n –eicosane was dispersed in 100 mL distilled water at 50 °C by adding 1.5 mL of a surfactant, and the mixture was stirred at 3000 rpm for 30 min to form a stable oil-in-water emulsion. Separately, CH polymer solution of 2.5% (w/v) was prepared by dissolving 0.6 gram of polymer in 2% acetic acid aqueous solution. The pH of the solution was measured as 4. Then, this solution was added in emulsion and coacervation between oppositely charge chitosan and CNPs was started to deposit the CNPs doped polymer around the core material. After 90 minutes, sodium hydroxide was added and pH was adjusted as 9 to complete coacervation reaction. In this step, reaction medium was diluted adding distilled water. After 30 minutes, reaction medium was cooled to 5 °C and hardening of microcapsules was carried out adding a 1.5 mL of cross-linker during 15 minutes. The microcapsules were treated with a 5% (w/v) aqueous solution of tannic acid for about 10 h at room temperature. The microcapsule preparation process was completed by repeated washings, filtering and drying of microcapsules. The stirring rate was kept constant at 3000 rpm for all process steps [21]. The chitosan:CNPs mass ratios were 1:2 and 1:1, while the shell:core material mass ratio was 1:1.5. The abbreviated names of the microcapsules and the amount of materials used were given in Table 1.

Table 1. Microcapsule samples

Microcapsule Name	CH/CNPs content (g)	n-Eicosane content (g)	Surface active material
MicroPCM-1	0.6 g./ 1.2 g.	2.7 g.	Span 20 - 1.5 mL
MicroPCM-2*	0.6 g./ 1.2 g.	2.7 g.	Span 80 - 1.5 mL
MicroPCM-3	0.6 g./ 1.2 g.	2.7 g.	Tween 20 - 1.5 mL
MicroPCM-4	0.6 g./ 1.2 g.	2.7 g.	Tween 40 -1.5 mL
MicroPCM-5	0.6 g./ 1.2 g.	2.7 g.	Tween 80 -1.5 ml
MicroPCM-6	0.6 g./ 0.6 g.	1.8 g.	Span 20 -1.5 mL
MicroPCM-7*	0.6 g./ 0.6 g.	1.8 g.	Span 80 -1.5 mL
MicroPCM-8	0.6 g./ 0.6 g.	1.8 g.	Tween 20 -1.5 mL
MicroPCM-9	0.6 g./ 0.6 g.	1.8 g.	Tween 40 -1.5 mL
MicroPCM-10	0.6 g./ 0.6 g.	1.8 g.	Tween 80 -1.5 mL
MicroPCM-11	0.6 g./ 0.6 g.	1.8 g.	Tween 20+tween 40 1 mL +1 mL

*: MicroPCM-2 and MicroPCM-7 were produced in our earlier studies and their characterization results were published as abstract [22]

2.3. Characterization of PCMs microcapsules

To characterize the thermal behavior of the microcapsule samples, DSC analyses were conducted on a Perkin Elmer Jade model instrument in the range of -10 - +80 °C at a heating or cooling rate of 10 °C.min^{-1} under nitrogen atmosphere. Furthermore, PCM content in microcapsule was determined according to the formula:

$$\text{Encapsulation Ratio (\%)} = \frac{\Delta H_{microcapsule}}{\Delta H_{n-eicosane}}.100$$

where $\Delta H_{microcapsule}$ is the enthalpy for the analyzed microcapsules (J/g) and seen in Figure 1 as Delta H value,

$\Delta H_{n-eicosane}$ is the enthalpy of the n-eicosane (J/g).

In order to identify the chemical structure of the microcapsules, spectroscopic analysis of samples, dispersed in KBr pellets, were performed on JASCO-430 Fourier Transform Infrared (FT-IR) Spectrophotometer in between the wave numbers of 4000 cm^{-1} and 400 cm^{-1}

The surface morphology of the fabricated capsules was investigated by optical microscopy (OM, Motic) instrument. Particle size was determined upon measuring more than 50 particles in OM images. SPSS 18.0 Statistics Software (SPSS Inc., Chicago, IL) was used for plotting particle size distribution (PSD) histograms of the results.

Thermo-gravimetric analysis (TGA) was conducted on a thermal analyzer (Seiko SII TG/DTA 7200) under a nitrogen atmosphere by heating the samples from 0°C to 400 °C at a heating rate of 10 °C/min.

2.4. Application of the MicroPCMs to the fabrics

MicroPCMs sample was applied to the cotton fabric by exhaustion methods. In the method, the fabrics were treated with bath containing the concentration of 35 % microcapsules in the presence of resin, catalyst, and softener, at 60 °C for 60 minutes on Gyrowash machine. The liquor ratio was 1:20. The concentration of resin, catalyst and softener was 60 g/L, 6 g/L, and 60 g/L, respectively.

2.5. Fabric Characterization

Scanning Electron Microscopy (SEM, LEO 440 Computer Controlled Digital) analysis was performed to determine the presence and distribution of microcapsules on the fabric surface. The fabric treated with microcapsules was washed on Gyrowash machine for 30 minutes at 40 °C, in accordance with TS EN ISO 105-C06-A2S. The washed samples were dried on oven at 40 °C following every cycle. The SEM analysis was repeated for the fabrics washed 5, 10, 20 and 30 times. The thermo-regulating effect of the fabric containing MicroPCM during heating was investigated by T-History system composed of a thermal camera (Fluke Ti100 Thermal Imager) and insulated polyurethane box. In the system, the temperature in air enclosure was increased instantaneously up to 50 °C and the temperature on the surface of the sample or reference fabrics placed in insulated box was recorded every 30 s during all test time. Before measurements, both of reference and sample fabrics treated with microcapsules were conditioned at 0 °C that is below the melting temperatures of the microcapsules. The surface temperature of the treated fabric and reference fabric were compared to evaluate thermal history results.

3. RESULTS AND DISCUSSIONS

3.1. DSC results of MicroPCMs

The thermal properties such as phase change enthalpy and temperature are the key parameters influencing the practical application of MicroPCMs. In this work, microcapsules containing n-eicosane were fabricated in chitosan/CNPs using a complex coacervation method. Furthermore, a series of surface active material was chosen to prepare microcapsules. The phase change properties of the microencapsulated PCM obtained from DSC analysis was given in Table 2. The DCS curves of the MicroPCM-2, MicroPCM-3 and MicroPCM-7 were given in Figure 1 as samples. As can be seen clearly in the tables, the melting and crystallization temperatures of the fabricated MicroPCMs were in the range of 35.43–36.81 °C and 31.04–35.43 °C, respectively. The melting points were consistent with the melting temperature of pristine n-eicosane, while solidification temperatures were generally higher. The melting enthalpy of the microcapsules were in the range of 66.19-120.51 J/g. Increased chitosan:CNPs ratio generally led to a higher encapsulation ratio. The encapsulation ratio % was calculated to be in the range of 23.93-43.56 %. The maximum melting enthalpy of 120.51 J/g, 104.54 J/g, and 104.21 J/g were obtained for MicroPCM-7, MicroPCM-3, and MicroPCM-2, respectively. According to Table 2, the maximum enthalpy values were generally obtained for the capsules prepared using Span 80 with 4.3 HLB and Tween 20 with 16.7 HLB. However, it was concluded that the prepared microcapsules in our study could be used for textile application in terms of proper phase transition temperatures and high latent heat storage capacities of them. As the results compared with literature, enthalpy values of the composite microcapsules containing inorganic material were as high as that of the organic walled microcapsules prepared by complex coacervation method [6, 12, 23]. It was concluded the n-eicosane was encapsulated by composite shell structure composed of organic chitosan and inorganic nano clay particles.

Table 2. Melting and crystallization behavior of microPCM samples and pure n-eicosane

Microcapsule Name	Melting Enthalpy (J/g)	Melting Temp. (°C)	Crystallization Enthalpy (J/g)	Crystallization Temp. (°C)	Encapsulation Ratio (%)
n-eicosane	276.65	36.73	-274.25	31.54	-
MicroPCM-1*	94.11	36.24	- 93.66	34.21	34.02
MicroPCM-2*	104.21	36.59	- 100.87	31.04	37.69
MicroPCM-3	104.54	36.74	-97.84	35.34	37.79
MicroPCM-4	79.75	36.56	-81.57	35.08	28.83
MicroPCM-5	89.31	36.63	-72.73	35.10	32.28
MicroPCM-6*	97.20	35.43	-90.63	33.72	35.13
MicroPCM-7*	120.51	35.53	-114.46	32.76	43.56
MicroPCM-8	68.64	36.81	-65.96	35.29	24.81
MicroPCM-9	67.75	36.41	-71.58	35.23	24.49
MicroPCM-10	68.25	36.63	-65.16	35.18	24.67
MicroPCM-11	66.19	36.74	-65.62	35.43	23.93

*: MicroPCM-1, MicroPCM-2, MicroPCM-6 and MicroPCM-7 were shown here for comparison [22]

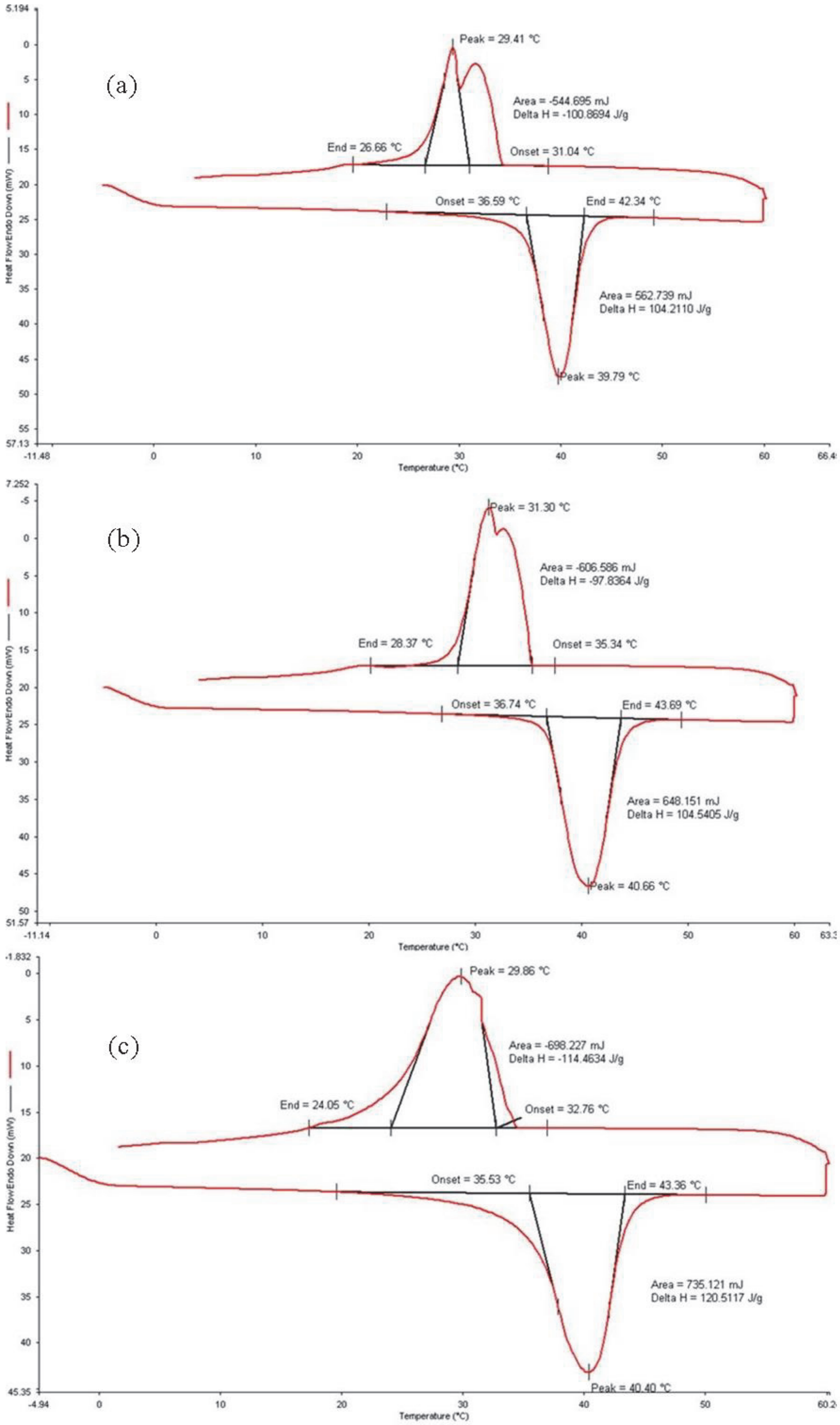

Figure 1. DSC curves of the microcapsule samples (a: MicroPCM-2, b: MicroPCM-3, c: MicroPCM-7)

3.2. TGA analysis of MicroPCMs

Thermal stability and thermal-degradation properties of the microcapsules were investigated with thermal gravimetric analysis (TGA). To investigate thermal degradation, three microcapsule samples having highest latent heat capacity were chosen. Figure 2 shows the thermal gravimetric analysis (TGA) curves of the microcapsules coded as MicroPCM-2, MicroPCM-3 and MicroPCM-7. In the curves, TG% value was used to determine the weight loss after thermal exposure. It could be clearly seen in these curves that approximately the same decompositions were observed in each of the three samples. Microcapsules degraded in 3 steps. Heating to 100 °C causes a slight decrease of the microcapsule weight, which may be due to thermal desorption of small molecules (e.g. H_2O) on the surface of microcapsules and a little release of n-eicosane [23] First small weight loss by releasing of the core material within the microcapsule during the heating process was shown up to 130 °C for MicroPCM-2, 124 °C for MicroPCM-3 and 150 °C for MicroPCM-7 and after that the second sharp step degradation occurred, indicating the core material n-eicosane released from the microcapsule. In this step, weight loss values in percent were 35 %, 41% and 28 % for MicroPCM-2, MicroPCM-3, and MicroPCM7, respectively. According to results given in Table 3, the residual weights % of the microcapsules were determined as 41 %, 34 % and 46 % at 400 °C for MicroPCM-2, MicroPCM-3, and MicroPCM7, respectively. Microcapsules produced using Span 80 showed less weight loss during the heating process due to Span 80 improved the encapsulation of the n-eicosane. According to the TGA analysis results, it was concluded that the compact membrane structure of the chitosan/CNPs microcapsules was thought to be responsible for good thermal stability. Besides, addition of CNPs to the shell structure caused to increase significantly thermal stability of the microcapsules. This finding was consistent with literature findings [19, 24, 25].

Table 3. Thermal degradation characteristics of MicroPCMs

Microcapsules	Degradation temperature interval (°C)	Weight loss %
MicroPCM-2	100-130 (1st step) 130-235 (2nd step) 235-400 (3rd step)	3.71 35 20
MicroPCM-3	100-124 (1st step) 124-227 (2nd step) 227-400 (3rd step)	2.5 41 25
MicroPCM-7	100-150 (1st step) 150-245 (2nd step) 245-400 (3rd step)	4.0 28 22

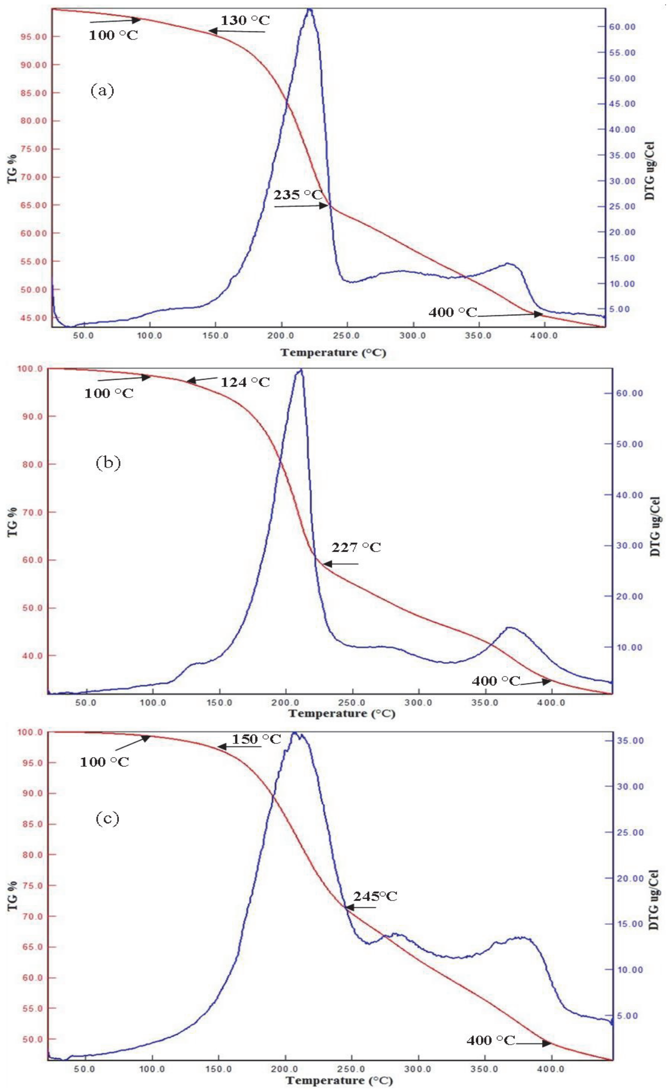

Figure 2. TGA curves of the microcapsule samples (a: MicroPCM-2 , b: MicroPCM-3 , c: MicroPCM-7)

3.3. Morphology and PSD of MicroPCMs

The morphology of the prepared microcapsules was investigated using OM analysis. As clearly seen from the OM images shown in Figure 3, all microcapsules were almost uniform and with spherical shapes. According to the PSD analysis results given in Figure 4, all of the MicroPCMs except MicroPCM-2 had generally bimodal distributions with the mean particle size of 0.42 µm and 0.43 µm for MicroPCM-1 and MicroPCM-6, 0.41 µm and 0.42 µm for MicroPCM-2 and MicroPCM-7, 0.53 µm and 0.46 µm for MicroPCM-3 and MicroPCM-8, 0.28 µm for MicroPCM-4 and MicroPCM-9, and 0.38 µm and 0.30 µm for MicroPCM-5 and MicroPCM-10, respectively. MicroPCM-11 had the mean particle size of 0.54 µm. According to the particle size measurement results, it could be concluded that all prepared capsules had nano-sizes and surface active materials with different HLB values had no significant effect on the size distribution mode and the average diameters of the capsules. On the other hand, the presence of clay nano particles could not be determined on the shell surface of the microcapsules. It was concluded that this was a result of the complex structure containing nano particles bound to polymer chains by electrostatic interactions [25].

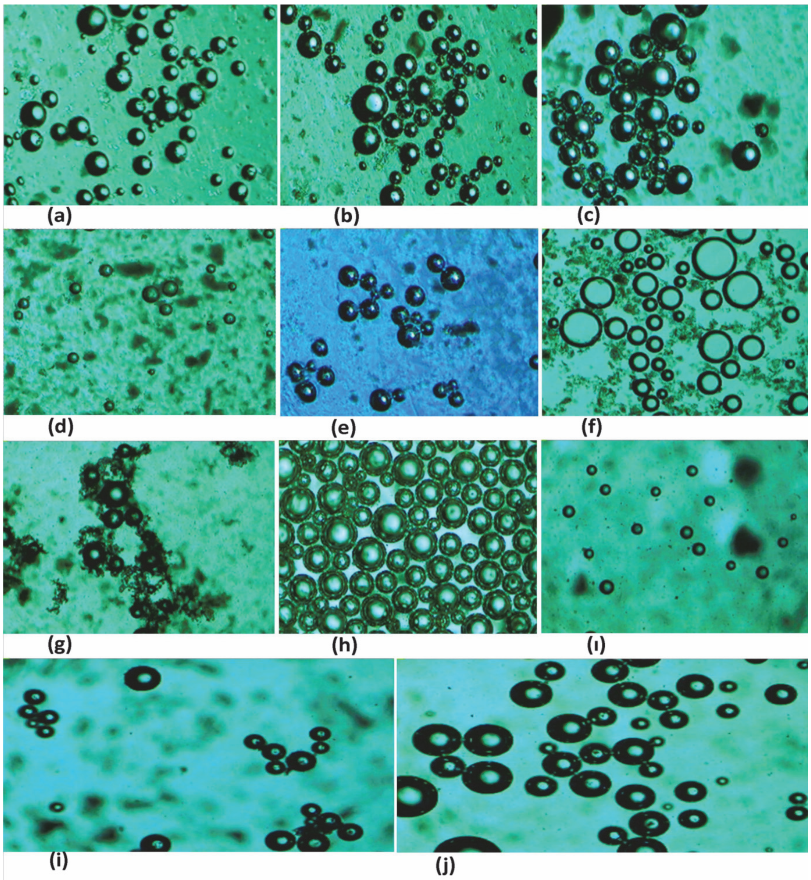

Figure 3. Optical microscope images of the microcapsules (a: MicroPCM-1; b: MicroPCM-2; c: MicroPCM-3; d: MicroPCM-4; e: MicroPCM-5; f: MicroPCM-6; g: MicroPCM-7; h: MicroPCM-8; ı: MicroPCM-9; i: MicroPCM-10; j: MicroPCM-11)

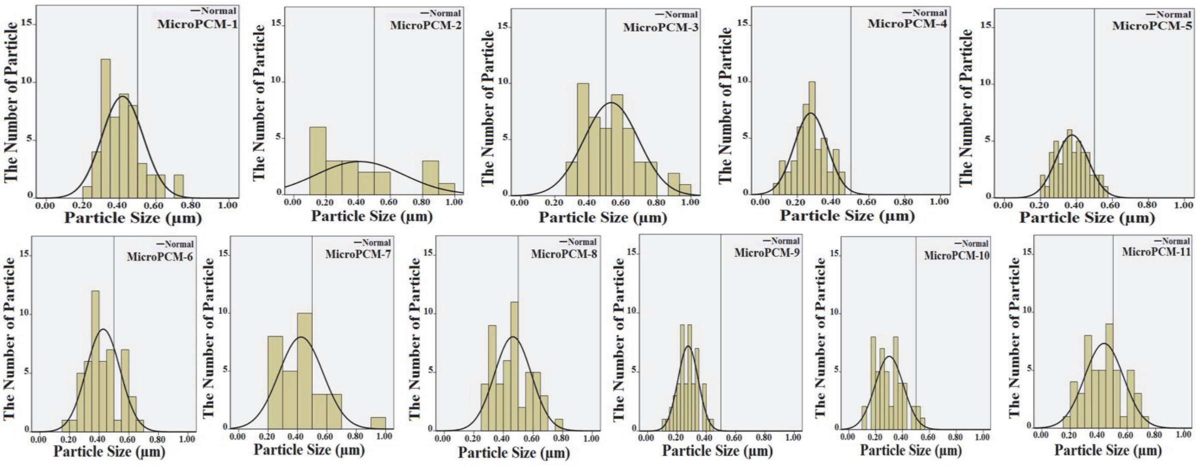

Figure 4. Particle size distribution diagrams of the MicroPCMs

3.4. FT-IR analysis of the MicroPCMs

The FT-IR spectra of chitosan, CNPs and the prepared microcapsules were given in Figure 5. Amides I and II of chitosan itself were located at 1660 cm^{-1} and 1591cm^{-1}, respectively [26]. The broad peak observed at 3200–3450 cm^{-1} had the contribution of different vibrations, namely the hydrogen-bonded OH stretching at 3448 cm^{-1}, and the NH_2 asymmetric stretching at 3295 cm^{-1}. The other peak at 2874 cm^{-1} and 1375 cm^{-1} were assigned to CH stretching and CH_3 symmetric deformation, respectively [27]. The characteristic peaks of the chitosan at 3200–3450 cm^{-1} arouse in the spectra of the microcapsules. Additionally, for MicroPCMs, the intensities of amide band I at 1660 cm^{-1} and amide band II at 1591 cm^{-1}, which can be observed clearly in pure chitosan, decreased. The peaks at 2915-2850 cm^{-1} in the spectra of the microPCMs were characteristic C-H peaks of the paraffin and they were proof the presence of the n-eicosane in MicroPCMs. The peak at 462 cm^{-1}in the spectra of the CNPs is an $Al\text{-}O_6$ stretching peak of the clay [28]. The spectra of all the MicroPCMs had this characteristic clay peak, which was a proof for CNPs in microcapsule structure.

3.5. SEM analysis of the MicroPCMs applied fabrics

The SEM images of the cotton fabric treated with MicroPCM-2 using exhaustion method were given in Figure 6. SEM images showed that microcapsules were distributed uniformly on the fiber surfaces without clustering. The amount of the microcapsules deposited on surface of the fabric decreased after repeated washings as seen from Figure 6b-e, respectively. However, the microcapsules on the fabric surface can be seen even after 30 times washes.

3.6. T-History results of the MPCM treated fabrics

To determine the cooling effect of the fabric sample treated with MicroPCM-2 due to heat absorption of PCM, T-history measurements was carried out. Figure 7 showed the T-History graphic of the fabrics treated with microPCM-2 by exhaustion method. As seen from Figure 7, the temperature curves of untreated reference and treated sample displayed considerable differences. The surface temperature of the microcapsule incorporated fabric was lower than that of the untreated reference. The difference in temperature reached up to 2.8 °C during measurement time which showed cooling effect of the microcapsule incorporated fabric. The thermo-regulating effect of the fabric decreased especially after one washing, but the effect still remained after five washings. However the thermo-regulating effect of the fabric disappeared after 10 washings.

4. CONCLUSIONS

Preparation and characterization of n-eicosane core and chitosan/CNPs shell microcapsules were carried out to find out their application possibility as textile additives. Morphological analysis results confirmed that n-eicosane was encapsulated in spherical Chitosan/CNPs particles. Their average particle diameters were at an interval of 0.28-0.54 µm. MicroPCMs could store 66-120 J/g and release 65-114 J/g latent heat energy which represented sufficient potential for thermal comfort applications in textiles. When MicroPCMs applied to cotton fabric by exhaustion methods, they distributed onto textile substrates homogeneously and durable to repeated washings. According to the T-history test results, it was determined that the fabrics treated with microcapsules had cooling effect.

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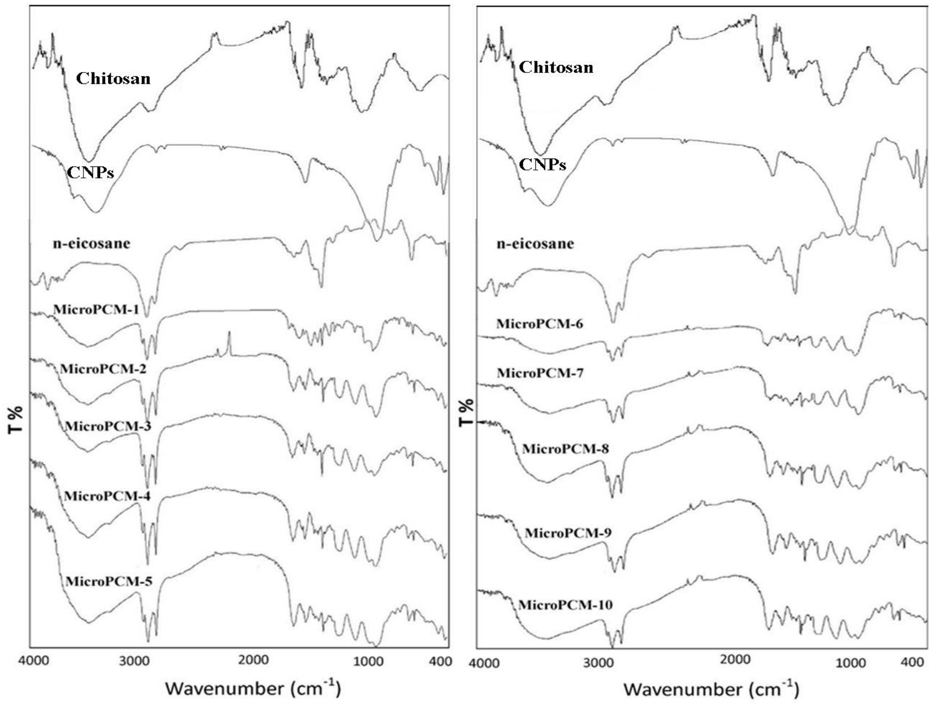

Figure 5. FT-IR spectra of the MicroPCMs

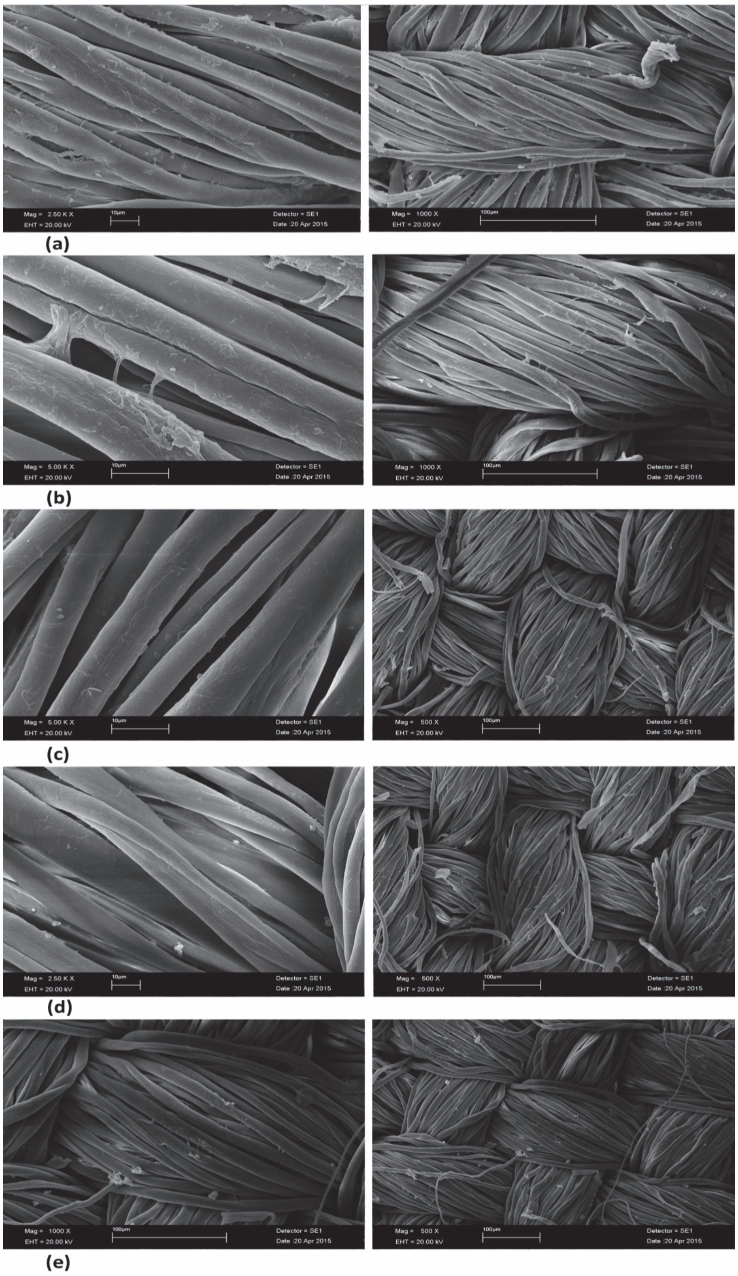

Figure 6. SEM images of the fabrics treated with microcapsules by exhaustion method (a: before washing, b:after five washings; c:after ten washings; d: after twenty washings; e: after thirty washings)

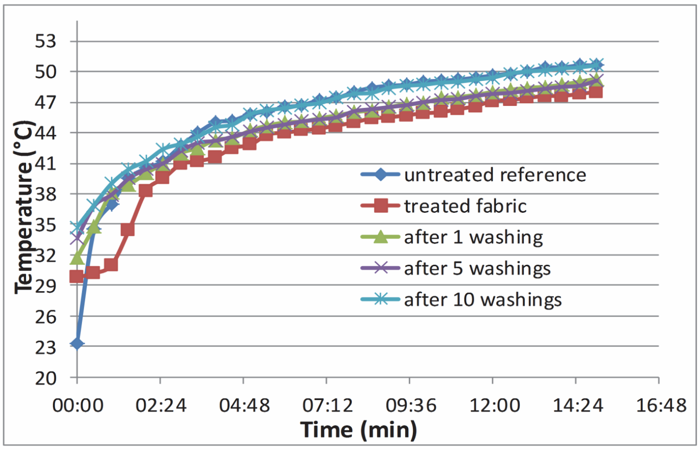

Figure 7. T-history graphic of the cotton fabric

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