(REFEREED RESEARCH)

INFLUENCE OF HYDROPHILIC COMONOMER ON THERMAL PROPERTIES OF POLYMETHYLEMETHACRYLATE/ N-ALKANES MICROCAPSULES

T POLİMETİLMETAKRİLAT/N-ALKANMİKROKAPSÜLLERİN TERMAL ÖZELLİKLERİNE HİDROFİLİK KOMONOMERİN ETKİSİ

Ruhan ALTUN ANAYURT[1], **Cemil ALKAN**[1,*], **Sennur ALAY AKSOY**[2],
Sena DEMİRBAĞ[2], **Müyesser Selda TÖZÜM**[2]

[1]*Gaziosmanpaşa University, Department of Chemistry, 60250Tokat, Turkey*
[2]*Süleyman Demirel University, Textile Engineering Department, 32260 Isparta, Turkey*

Received: 17.11.2016 Accepted: 05.03.2017

ABSTRACT

A series of poly(MMA-co-2-HEA)/n-octadecane (P(MMA-co-2HEA)/C18) and poly(MMA-co-2-HEA)/n-eicosane (P(MMA-co-2HEA)/C20) microcapsules were prepared by an emulsion polymerization method as microencapsulated phase change materials (MEPCMs). The structural identification was done by using FTIR spectroscopy and thermal properties of the hydrophilic monomer imcorporated microcapsules were investigated using Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) techniques. The surface morphology and particle size of MEPCMs were studied using a Polarised Optical Microscope (POM) and a Particle Size Analysizer (PSA) respectively. DSC indicated that the microcapsules containing highest amount of the n-alkane had a latent heat of 125 J/g as and TGA technique showed about thermal stability. The particle size and distribution analysis showed that the microcapsules had uniform and narrow size distrubiton. Also it was confirmed by FTIR spectroscopy that the poly(MMA-co-2-HEA) shell was successfully synthesized as the shell of the paraffin core. Besides it was found that the thermo-physical properties were strongly dependant on the content of the microcapsules.

Keywords: Polymer synthesis, phase change materials (PCMs), microencapsulated PCMs, PMMA, copolymer.

ÖZET

Mikrokapsüllenmiş faz değiştiren material (MEPCMs) olarak, poli(metil metakrilat-ko-2 hidroksi etil akrilat)/n-oktadekan (P(MMA-co-2HEA)/C18) ve poli(metil metakrilat-ko-2 hidroksi etil akrilat)/n-eykosan mikrokapsüller emülsiyon polimerizasyonu metodu ile üretilmiştir. Hidrofilik monomer ilave edilmiş mikrokapsüllerin yapıları, FT-IR spektroskopisi ile aydınlatılmış ve termal özellikleri diferansiyel taramalı kalorimetre (DSC) ve termogravimetrik analiz (TGA) teknikleri ile araştırılmıştır. Mikrokapsüllenmiş faz değiştiren maddelerin yüzey morfolojileri ve parçacık boyutu polarize ışık mikroskobu (POM) ve parçacık analiz edici system (PSA) ile incelenmiştir. DSC tekniği mikrokapsüllerin en fazla 125 J/g enerji depoladığını gösterirken TGA tekniği kararlılıklarını göstermiştir. Parçacık boyutu ve dağılımı analizi mikrokapsüllerin düzenli ve dar aralıklı dağılıma sahip olduğunu göstermiştir. FT-IR spektroskopisi paraffin çekirdeğin etrafında poli(MMA-ko-2-HEA) duvarın başarılı bir şekilde sentezlendiğini göstermiştir. Bunun yanında mikrokapsüllerin termo-fiziksel özelliklerinin mikrokapsül içeriğine şiddetli derecede bağlı olduğu bulunmuştur.

Anahtar Kelimeler: Polimer sentezi, faz değiştiren maddeler (FDMler), mikrokapsüllenmiş FDMler, PMMA, kopolimer.

1. INTRODUCTION

Phase change materials (PCMs) are substances which are able to store and release large amounts of latent heat energy during phase change process [1]. Among the PCMs, *n*-alkanes are a widely used organic PCMs and have several advantages such as high latent heat capacity, suitable phase change temperature, little or no super cooling, volumetric stability, good chemical and thermal

---

Corresponding Author: Cemil Alkan e-mail: cemil.alkan@gop.edu.tr

stability, and nontoxicity [2-4]. Yet, some problems have been observed related to the leakage, odour, and evaporation when utilized without encapsulation. Microencapsulation technology is a recent development and an approach for the prevention of the leakage and of the problems mentioned above [5–8].

Microencapsulated PCMs (MEPCMs) are polymeric particles utilizing for storage of thermal energy. Microencapsulated phase change energy storage systems have usually been composed of three active ingredients: a PCM in the core, a polymer in the shell and a crosslinking agent to mantain the system's consistency. It is possible to produce microcapsules with thermal energy storage property using different PCMs and polymers. Generally n-alkane waxes (linear long chain hydrocarbons) have been encapsulated using polymers such as polystyrene, poly(methyl methacrylate), melamine-formaldehyde, polyurea-formaldehyde, polyurea, and gelatin/arabic gum [9-15].

One of the recent MEPCM systems is composed of n-alkane as core material, poly(methylmethacrylate) (PMMA) as shell and ethylene glycole dimethacrylate (EGDM) as a crosslinking agent [16,17]. PMMA shell is attractive in the encapsulation of PCMs due to its being transparent, lightweight, easy processable, environmentally stable, non-toxic, and low cost [17-36]. Recently, microcapsules containing n-alkanes with different methylmethacrylate (MMA)-based copolymer shells have been produced. Acrylic acid (AA) [16], butyl acrylate (BA), butyl methacrylate (BMA), lauryl methacrylate (LMA) and stearyl methacrylate (SMA) [24], have been employed as monomers to copolymerize with MMA. In this study, parafinic PCMs such as n-octadecane and n-eicosane that can function at different temperatures have been microencapsulated by MMA-based copolymer in order to produce microcapsules storing thermal energy. In the study, 2HEA monomer was employed as comonomer to MMA for functinality. Microcapsules with reactive groups on their outer surface improving their adhesion to substances like textiles, foams, papers, etc. through physical interactions were aimed. The particles could also be validated to bind them on to the possible substrates using bridging chemicals through synthetic routes.

Experimental

Materials

N-alkanes (n-octadecane and n-eicosane, Alfa Aesar) as PCMs were of analytical grade and used as received. Methylmethacrylate (MMA) (Merck) and 2-hydroxyethyl acrylate (2HEA) (Sigma Aldrich) monomers were used to synthesize co-polymer shells of microcapsule and used as recived. Ethylene glycol dimethacrylate (Merck) was used as cross-linker. Triton X-100 (Merck) as emulsifier was used as received. Ferrous sulfate heptahydrate (Sigma Aldrich) and ammonium persulfate (Riedel-de haen) were also of analytical grade and used without further purification. A 70 % tert-butyl hydroperoxide was obtained from Merck Company and used as received.

Preparation of microcapsules

MMA (100 g), 2HEA (1, 5, and 10 g in each of 3 different products), ethylene glycol dimethacrylate (10 g), and n-alkane (100 g) were assembled as oil phase in emulsion system in a total of 400 mL deionized water. Oil phase was emulsified using 10 g of Triton X-100 (surfactant). Suitable mixing speed was determined as 1000 rpm according to our experiences. The reaction mixture was homogenized at 50 °C using a mechanical homogenizer. Reaction was initiated by the addition of 1 g of ammonium persulphate powder ($(NH_4)_2S_2O_8$) and 8 mL freshly prepared $FeSO_4•7H_2O$ solution. Ferrous sulfate solution was prepared by adding 0.15 g $FeSO_4•7H_2O$ into 100 mL deionized water. The reaction medium was heated to 80 °C and maintained at that temperature for 30 minutes with stirring at 500 rpm. The reaction was continued for five hours at the same temperature and stirring speed. The colloidal emulsion was concentrated by evaporation of the water phase and the precipitate was dried under vacuum at 40 °C. The microencapsulation of PCMs was carried out in a 500 mL three neck round-bottomed flask with a mechanical stirrer for emulsion polymerization. The preparation conditions and the corresponding adopted nomenclature of the microcapsules were summarized in Table 1.

Table1. The preparation conditions and corresponding adopted nomenclature of the microcapsules

Microcapsule	Hydroxyethylacrylate percentage	Abbreviation
Poly(MMA-co-2HEA)/hexadecane[37]	1	P(MMA-co-2HEA)/C16-1
Poly(MMA-co-2HEA)/hexadecane[37]	5	P(MMA-co-2HEA)/C16-5
Poly(MMA-co-2HEA)/hexadecane[37]	10	P(MMA-co-2HEA)/C16-10
Poly(MMA-co-2HEA)/octadecane[38]	1	P(MMA-co-2HEA)/C18-1
Poly(MMA-co-2HEA)/octadecane[38]	5	P(MMA-co-2HEA)/C18-5
Poly(MMA-co-2HEA)/octadecane[38]	10	P(MMA-co-2HEA)/C18-10
Poly(MMA-co-2HEA)/eicosane	1	P(MMA-co-2HEA)/C20-1
Poly(MMA-co-2HEA)/eicosane	5	P(MMA-co-2HEA)/C20-5
Poly(MMA-co-2HEA)/eicosane	10	P(MMA-co-2HEA)/C20-10

37: P(MMA-co-2HEA)/C16 microcapsules were previously synthesized in our laboratory and they are shown here for comparison[37]

38:P(MMA-co-2HEA)/C18 microcapsules were also synthesized in our laboratory and reported as a poster presentation[38].

Microcapsules characterization

Thermal properties of MEPCMs were investigated using a differential scanning calorimeter (DSC, Perkin-Elmer Jade) with a heating-cooling cycle between -5 °C and 80 °C at 5 °Cmin^{-1} under nitrogen athmosphere flowing at 60 mLmin^{-1}. The spectroscopic measurements of the MEPCMs were performed with KBr disks using a FT-IR instrument (Jasco 430) between 4000-400 cm^{-1}. Samples were mixed with KBr and pressed as pellets. The particle sizes of microcapsules were measured using a particle size analyzer instrument (Malvern MS2000 E). MEPCMs were stirred in distilled water at 10000 rpm using mechanical stirrer for 45 minutes to avoid clustering before testing. The surface morphology of the fabricated capsules was examined using a polarized optical microscopy (POM) instrument. Thermal degradation temperatures and steps were determined on a thermogravimetric analyzer (PERKIN-ELMER TGA7). The thermogravimetry analysis (TGA) instrument was calibrated with calcium oxalate between 25 and 600 °C at a heating rate of 10 °Cmin^{-1} in a static air atmosphere prior to measurements. DTG (Differential Thermogravimetry) was calculated with the instrument software and reported to reveal weight losses clearly.

Results and Discussion

Three series as MEPCMs were prepared. Each of the series comprised of different co-monomer HEA ratios. MEPCMs were analysed using common characterisation techniques.

Infrared spectroscopy

The structure of the shell polymer was analyzed by FT-IR spectra which were used to prove the synthesis also. For this reason, the spectra of the ingredient monomers and the microcapsules were given in Figure 1 and tabulated in Table 2. N-alkane waxes, which were used in this study, have very similar spectra and are characterized by absorptions due to C–H stretching and bending. In the spectrum of n-alkane waxes, a double peak at 2900–2840 cm^{-1} was due to the alkyl C–H stretching vibrations of aliphatic groups and C-H bending vibrations at 1459 and 1375 cm^{-1} were due to methylene bridges. Additionally, the characteristic absorption peak at 717 cm^{-1} corresponded to the in-plane rocking vibration of the methylene group [39, 40]. Each of the characteristic peaks belonging to the core material preserves itself after microencapsulation.These results confirmed that the succesful encapsulation of n-alkane waxes could be carried out within P(MMA-co-2HEA) shell. The characteristic C=C peak was invisible in the spectra of microcapsules, while it arised at 1639 cm^{-1} and at 1627 cm^{-1} in the spectra of MMA and 2HEA monomer, respectively. This means that polymerization was carried out between the monomers.

Furthermore, a strong peak near 1727 cm^{-1}-1731 cm^{-1} in the spectra of the microcapsules corresponds to the overlapping peak of the carbonly (C=O) group of 2HEA (at 1718 cm^{-1}) and MMA (at 1741 cm^{-1}). The peak at 3430 cm^{-1} in the spectra 2HEA, which is a H-bonded –OH group peak, arises at near 3430-3450 cm^{-1} in the spectra of the microcapsules. This peak was a proof for the presence of the functional hydroxyl group on the microcapsule structure. These results confirmed the formation of a microcapsule shell consisting of P(MMA-co-2HEA) copolymer.

Differential scanning calorimetry

The thermograms of MEPCMs determined using a DSC are shown in Figure 2 and the data recorded is given in Table 3. As can be seen clearly from the table, melting and crystallization temperatures of the prepared microcapsules are in the range of 26.9-27.2 °C and 24.3-25.9°C for P(MMA-co-2HEA)/C18, 35.6-35.7 °C and 35.2-35.4 °C for P(MMA-co-2HEA)/C20 microcapsules. The thermal properties obtained from the DSC analysis indicated that P(MMA-co-2HEA)/C18 microcapsules stored the latent heat in the range of 69.7-125.1 J/g and released it in the range of -66.5- (-123.1) J/g, respectively. The latent heats of melting and crystalliation of the P(MMA-co-2HEA)/C20 microcapsules were in the range of 69.3-125.3 J/g and -64.9- (-115.9) J/g, respectively.

In microcapsulation applications, the phase-change performance of MEPCMs were also characterised by the encapsulation ratio in percent (ER), which can be calculated using the following equation;

$$ER = \frac{\Delta\mathrm{H}_{microcapsule}}{\Delta\mathrm{H}_{PCM}} x100$$

Where $\Delta\mathrm{H}microcapsule$ and $\Delta\mathrm{H}_{PCM}$ are melting enthalpies of microcapsules and pure n-alkane, respectively.The encapsulation ratio describes the efficient encapsulation percentage of PCM in the shell. According to the Table 3 the calculated encapsulation ratio were in the range of 22-34 wt% for P(MMA-co-2HEA)/C16, 28-51% for P(MMA-co-2HEA)/C18, and 25-45% for P(MMA-co-2HEA)/C20 MEPCMs. According to these results, the phase transition temperatures and enthalpy values for the MEPCMs developed are not drastically affected by the hydrophilic comonomer content and it is still possible to adjust the encapsulation ratio of the microcapsules.

In some of the samples the enthalpy was found less than theoretical yield which can be explained by evaporation of some of the monomers during the reaction in the open system under hood. Also it was possibly due to the negative effect of hydrophilic comonomer during shell formation.

Thermogravimetric analysis

TGA curves of the P(MMA-co-2HEA)/C18-10 and P(MMA-co-2HEA)/C20-10MEPCMs were given in Fig. 3, and the degradation temperatures and % mass loss values of MEPCMs were presented in Table 4. Fig. 3 showed that MEPCMs degraded in three-step thermal degradation processes.The first stage occurred between 80-190 °C for P(MMA-co-2HEA)/C16 MEPCMs, 90-195 °C for P(MMA-co-2HEA)/C18 MEPCMs, and 100-220 °C for P(MMA-co-2HEA)/C20 MEPCMs respectively. The first step was due to evaporation from the shell and evaporation of n-alkane from the core.The second and third weight losses of the MEPCMs were attributed to the further decompositions of the shell. Because that the shell is crosslinked, the degradation occurred in a range rather than a constant temperature normally. As can be seen from the data in Table 4, the MEPCMs decomposed totally before 420°C. These results showed that P(MMA-co-2HEA) shell is thermal stable at higher temperatures than possible ambient. In addition, TGA analysis consisted with the core/shell ratio calculated from DSC data.

Table 2. The wavelengths belong to monomer and microcapsules.

2HEA	3430 cm^{-1}	O-H stretching peak
	2954 cm^{-1}	C-H stretching peak
	1718 cm^{-1}	Carbonyl peak
	1627 cm^{-1}	-C=C- stretching peak
	1300 cm^{-1}-1000 cm^{-1}	-C-O- stretching peaks
MMA	1741 cm^{-1} 1100-	stretching peak of carbonyl group,
	1300 cm^{-1} 1639 cm^{-1}	-C-O- stretching peaks on ester C=C peak
n-octadecane (C18)	2919 cm^{-1} -2859cm^{-1}	C-H stretching peak
	1459 cm^{-1}-1369cm^{-1}	C-H bending peak
	717 cm^{-1}	C-H rocking vibration
P(MMA-co-2HEA)/C18-1	3440 cm^{-1}	O-H stretching peak
	2954 cm^{-1}	C-H stretching peak
	2921 cm^{-1} - 2850 cm^{-1}	C-H stretching peak of n-alkane
	1727 cm^{-1}	C=O stretching peak
	1471cm^{-1}- 1388 cm^{-1}	characteristic peaks of n-alkane
	1247 cm^{-1} -1149 cm^{-1}	-C-O- stretching peaks
P(MMA-co-2HEA)/C18-5	3430 cm^{-1}	O-H stretching peak
	2952 cm^{-1}	C-H stretching peak
	2921 cm^{-1} - 2850 cm^{-1}	C-H stretching peak of n-alkane
	1727 cm^{-1}	C=O stretching peak
	1471cm^{-1}- 1367 cm^{-1}	characteristic peaks of n-alkane
	1243 cm^{-1} -1149 cm^{-1}	-C-O- stretching peaks
P(MMA-co-2HEA)/C18-10	3451 cm^{-1}	O-H stretching peak
	2952 cm^{-1}	C-H stretching peak
	2923 cm^{-1} - 2852 cm^{-1}	C-H stretching peak of n-alkane
	1729 cm^{-1}	C=O stretching peak
	1452cm^{-1}- 1388 cm^{-1}	characteristic peaks of n-alkane
	1245 cm^{-1} -1149 cm^{-1}	-C-O- stretching peaks
n-eicosane (C20)	2917 cm^{-1} -2840cm^{-1}	C-H stretching peak
	1467 cm^{-1}-1375cm^{-1}	C-H bending peak
	721 cm^{-1}	C-H rocking vibration
P(MMA-co-2HEA)/C20-1	3432cm^{-1}	O-H stretching peak
	2954cm^{-1}	C-H stretching peak
	2915cm^{-1}-2848 cm^{-1}	C-H stretching peak of n-alkane
	1727 cm^{-1}	C=O stretching peak
	1471 cm^{-1}-1388 cm^{-1}	characteristic peaks of n-alkane
	1245 cm^{-1}-1149 cm^{-1}	-C-O- stretching peaks
P(MMA-co-2HEA)/C20-5	3444cm^{-1}	O-H stretching peak
	2952cm^{-1}	C-H stretching peak
	2915cm^{-1}-2848 cm^{-1}	C-H stretching peak of n-alkane
	1731 cm^{-1}	C=O stretching peak
	1471 cm^{-1}-1388 cm^{-1}	characteristic peaks of n-alkane
	1243 cm^{-1}-1149 cm^{-1}	-C-O- stretching peaks
P(MMA-co-2HEA)/C20-10	3444cm^{-1}	O-H stretching peak
	2954cm^{-1}	C-H stretching peak
	2915cm^{-1}-2848 cm^{-1}	C-H stretching peak of n-alkane
	1731 cm^{-1}	C=O stretching peak
	1471 cm^{-1}-1388 cm^{-1}	characteristic peaks of n-alkane
	1243 cm^{-1}-1149 cm^{-1}	-C-O- stretching peaks

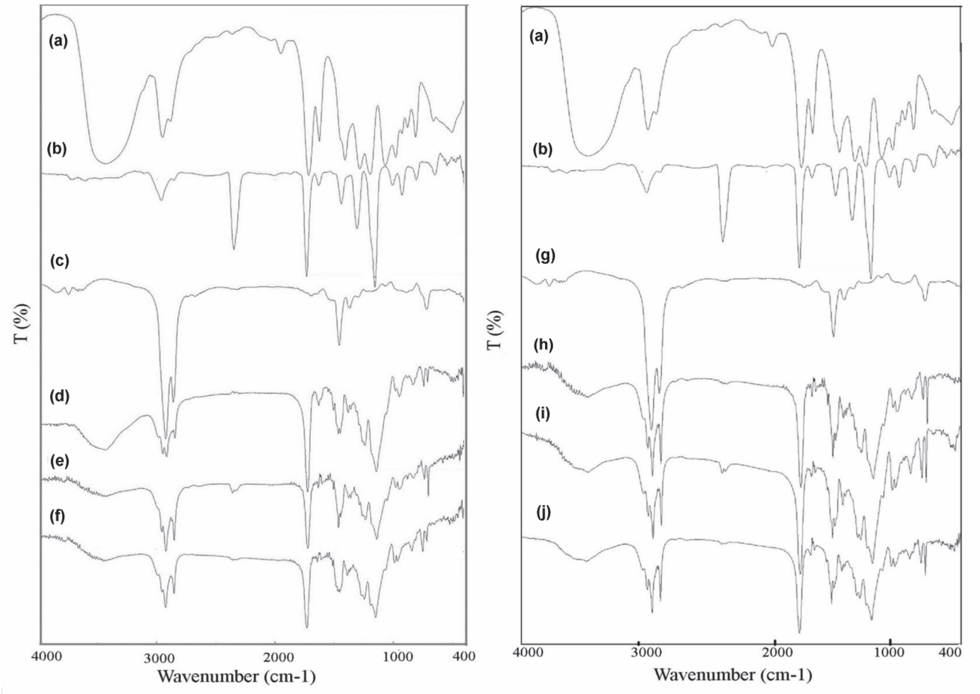

Figure 1. FT-IR spectra of (a): 2HEA; (b): MMA; (c): n-octadecane (C18); (d): P(MMA-co-2HEA)/C18-1; (e): P(MMA-co-2HEA)/C18-5; (f): P(MMA-co-2HEA)/C18-10; (g): n-eicosane (C20); (h:)P(MMA-co-2HEA)/C20-1; (i): P(MMA-co-2HEA)/C20-5; (j): P(MMA-co-2HEA)/C20-10 microcapsules

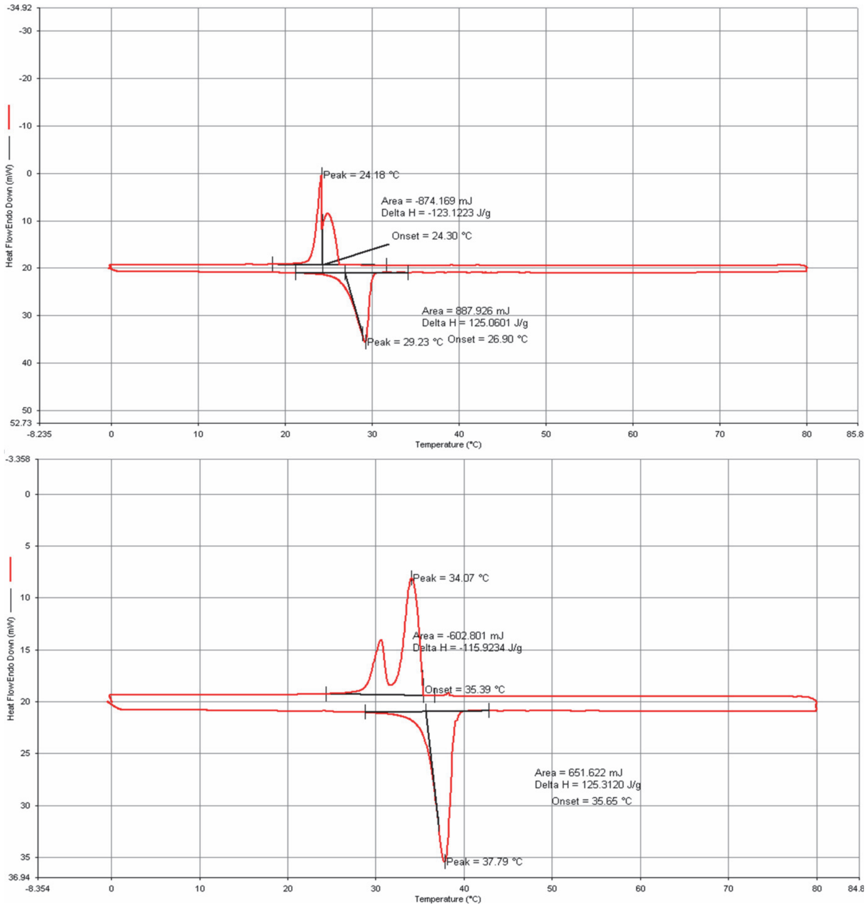

Figure 2. DSC thermogram of P(MMA-co-2HEA)/C18-1 (on top) and P(MMA-co-2HEA)/C20-1 MEPCMs (at the bottom)

Table 3. DSC results of P(MMA-co-2HEA)/n-alkane MEPCMs

Microcapsule	Melting Enthalpy (J/g)	Melting Temp. (°C)	Crystallization Enthalpy (J/g)	Crystallization Temp. (°C)	Encapsulation Ratio (%)
P(MMA-co-2HEA)/C16-1[37]	105.2	17.5	-107.2	15.6	34
P(MMA-co-2HEA)/C16-5[37]	68.3	16.9	-68.7	15.1	22
P(MMA-co-2HEA)/C16-10[37]	105.7	17.5	-105.3	16.1	34
P(MMA-co-2HEA)/C18-1	125.1	26.9	-123.1	24.3	51
P(MMA-co-2HEA)/C18-5	121.3	27.2	-121.2	25.9	49
P(MMA-co-2HEA)/C18-10	69.7	26.9	-66.5	25.9	28
P(MMA-co-2HEA)/C20-1	125.3	35.7	-115.9	35.4	45
P(MMA-co-2HEA)/C20-5	69.3	35.7	-64.9	35.2	25
P(MMA-co-2HEA)/C20-10	95.3	35.6	-86.5	35.2	34

37: P(MMA-co-2HEA)/C16 microcapsules were previously synthesized in our laboratory and they are shown here for comparison[37]

Table 4. TGA data of P(MMA-co-2HEA)/n-alkane MEPCMs

Microcapsule	Degradation interval (°C)	% Mass loss
P(MMA-co-2HEA)/C16-1	80-175 (1.step)	4
	175-275 (2.step)	13
	275-410 (3.step)	82
P(MMA-co-2HEA)/C16-5[37]	80-160 (1.step)	4
	160-350 (2.step)	78
	350-425 (3.step)	18
P(MMA-co-2HEA)/C16-10	80-180 (1.step)	41
	180-275 (2.step)	7
	275-420 (3.step)	52
P(MMA-co-2HEA)/C18-1	90-180 (1.step)	9
	180-310 (2.step)	40
	310-430 (3.step)	48
P(MMA-co-2HEA)/C18-5	90-195 (1.step)	36
	195-275 (2.step)	9
	275-430 (3.step)	55
P(MMA-co-2HEA)/C18-10	90-170 (1.step)	9
	170-320 (2.step)	50
	320-430 (3.step)	38
P(MMA-co-2HEA)/C20-1	100-220 (1.step)	45
	220-310 (2.step)	30
	310-420 (3.step)	23
P(MMA-co-2HEA)/C20-5	100-220 (1.step)	33
	220-305 (2.step)	45
	305-420 (3.step)	21
P(MMA-co-2HEA)/C20-10	100-230 (1.step)	47
	230-300 (2.step)	20
	300-420 (3.step)	32

Particle Size Analysis (PSA)

Figs. 4 and 5 showed the polarised optical microcopy images and particle diameter distribution diagrams of the P(MMA-co-2HEA)/C18 and P(MMA-co-2HEA)/C20 MEPCMs. As shown from particle size distribution diagrams the synthesized capsules had bimodally distributed with less than 20 µm particle size. This may because of the response of two the polymer with different kinds of monomers in the shell that the particles scatter the light to two close positions. The mean particle sizes of the microcapsules for P(MMA-co-2HEA)/C18-1-10 were 17.5µm, 11.6 µm, and 15.2 µm, respectively as those of P(MM-co-2HEA)/C20-1-10 were also 16.4µm, 18.0 µm and 14.5 µm, respectively. Consequently hydrophilic co-monomer has no considerable effect on the average sizes and its distribution.

Polarised Optical Microscopy (POM) Analysis

Particle size and its distribution may be critically important for MEPCM manufacturing. Thus they should be monitored after each synthesis. POM is not a sensitive technique for the particle size detection but it is considerably cheap and easy to apply as compared to SEM and PSD. Besides POM shows the geniune sizes of the particles as PSD may picturize coagulated domains and SEM requires a great care. Therefore, a morphological investigation was conducted to compare microscopic analysis with PSD. POM images given in Figure 4 and Figure 5 (a,b,c) clearly illustrate that the MEPCMs consisted with the PSD data.They show that MEPCMs were spherical in shapes with smooth and compact surface. In addition according to POM, the amount of hydrophilic comonomer had no significant effect on the microcapsule morphology.

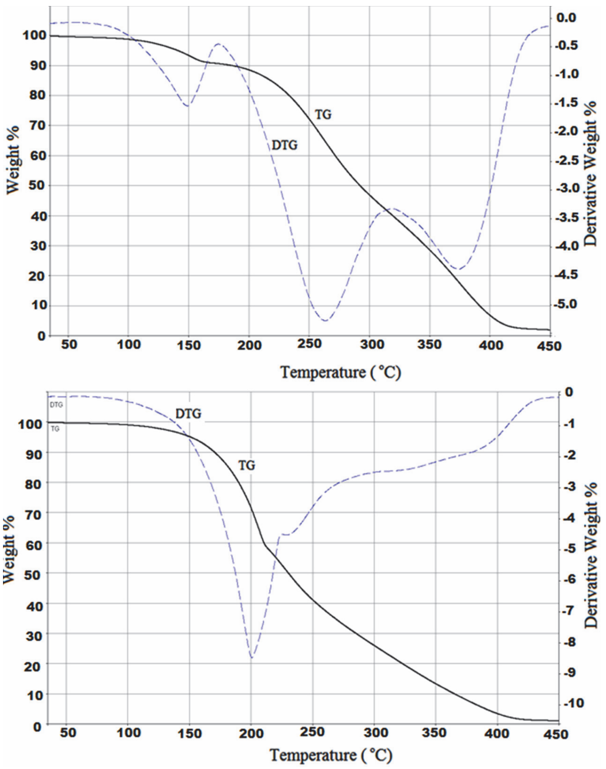

Figure 3. TGA termogram of P(MMA-co-2HEA)/C18-10 (above) and P(MMA-co-2HEA)/C20-10 (below) microcapsules

Conclusion

In this study, microcapsules with P(MMA-co-2HEA) shell and n-alkane core were produced via emulsion polymerization. The produced microcapsules were capable of absorbing 125.3-68.3 J/g and releasing -123.1 - -64.9 J/g of heat. According to the FT-IR results, microcapsules with 2HEA comonomer in the structure had functional hydroxyl groups on the backbone of the copolymer. The presence of n-alkane in the microcapsules was also proven by FT-IR spectroscopy analysis and DSC analysis. The data obtained from particle size analysis indicated that MEPCMs were obtained with a narrow size distribution between 11.6 and 18 µm. Additionally POM analysis showed that microcapsules were almost spherical in shape. MEPCMs produced in this project are very important because that they have functional groups on the outer surface to interact or bind to some matrices such as paints, foams, papers, and textiles. Therefore they can be used as thermal comfort additives in building, health, agriculture, food and textile.

Acknowledgements

The author would like to acknowledge the financial support by Scientific and Technological Research Council of Turkey (TUBITAK) (Project no.: 111M484).

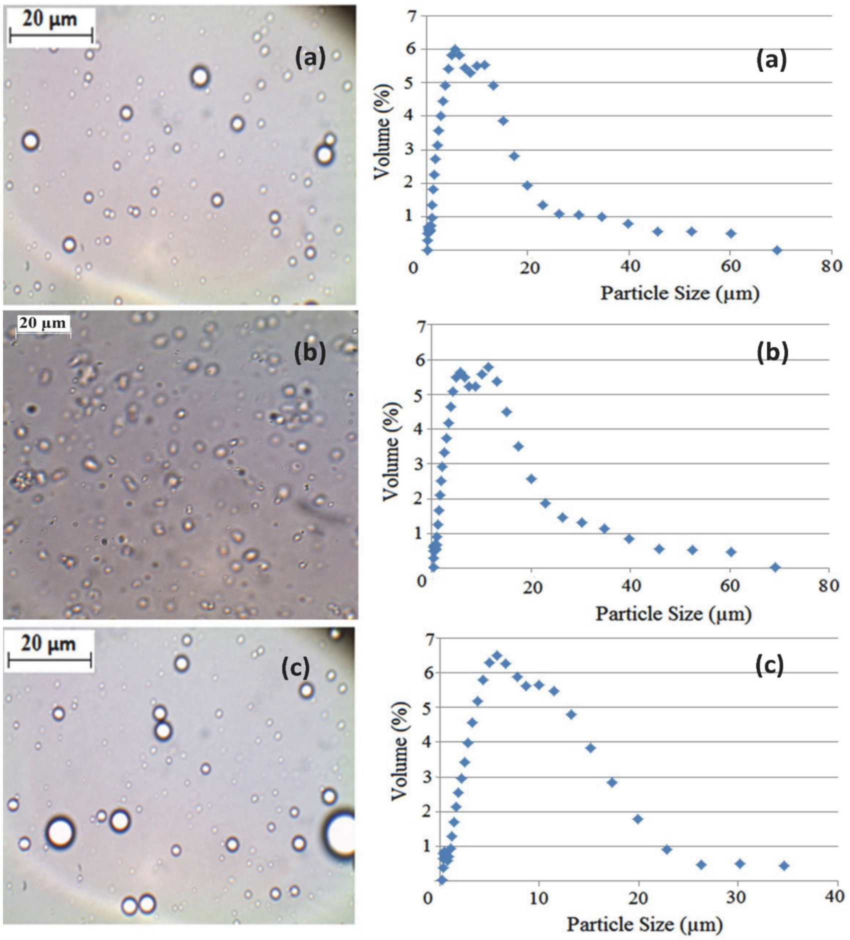

Figure 4. POM images and particle size distribution curves of P(MMA-co-2HEA)/C18-1 (a), P(MMA-co-2HEA)/C18-5, (b), and P(MMA-co-2HEA)/C18-10 (c).

Table 5. Particle size ranges and mean particle sizes of P(MMA-co-2HEA)/n-alkane microcapsules

Microcapsules	Intensive particle size range in µm	The mean particle size in µm
P(MMA-co-2HEA)/C18-1	2-17	17.5
P(MMA-co-2HEA)/C18-2	1.5-10.5	11.6
P(MMA-co-2HEA)/C18-3	2-17	15.2
P(MMA-co-2HEA)/C20-1	2-18	16.4
P(MMA-co-2HEA)/C20-2	2-19	18.0
P(MMA-co-2HEA)/C20-3	5-15	14.5

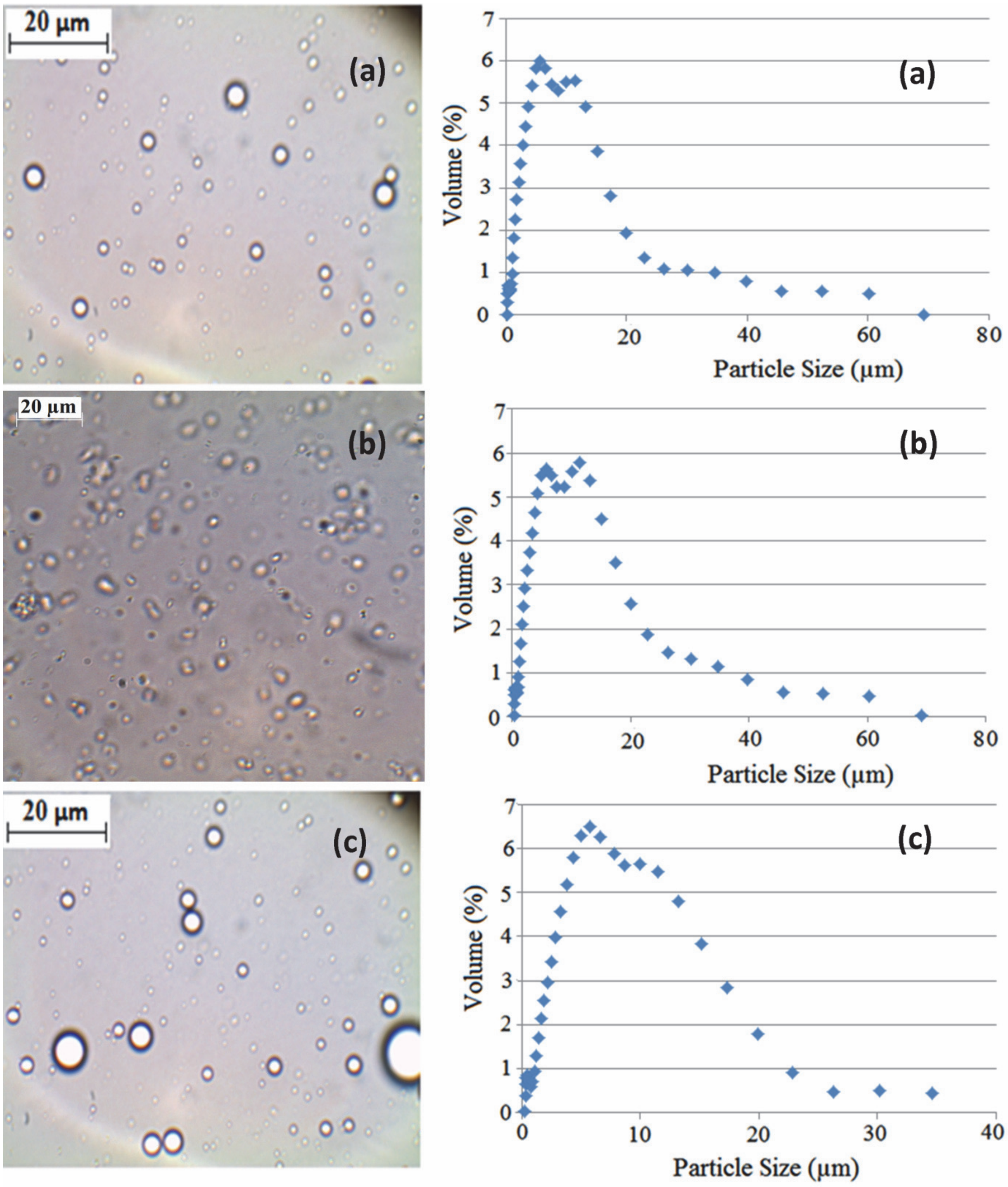

Figure 5. POM images and particle size distribution curves of P(MMA-co-2HEA)/C20-1 (a), P(MMA-co-2HEA)/C20-5 (b), and P(MMA-co-2HEA)/C20-10 (c).

REFERENCES

1. Chai L., Wang X. and Wu D., 2015,“Development of Bifunctional Microencapsulated Phase Change Materials With Crystalline Titanium Dioxide Shell For Latent-Heat Storage And Photocatalytic Effectiveness”, Applied Energy, Vol:138, pp:661–674.
2. Sarı A., Alkan C., Kahraman-Döğüşcü D. and Kızıl Ç, 2015,“Micro/Nano Encapsulated *N*-Tetracosane And *N*-Octadecane Eutectic Mixture With Polystyrene Shell For Low-Temperature Latent Heat Thermal Energy Storage Applications”, Solar Energy, Vol:115, pp:195–203.
3. Qiu X., Lu L., Wang J., Tang G. and Song G., 2015“Fabrication, Thermal Properties and Thermal Stabilities of Microencapsulated *N*-Alkane with Poly(Lauryl Methacrylate) As Shell”, Thermochimica Acta, Vol:620, pp: 10–17.
4. Tang X., Li W., Zhang X. and Shi H., 2014,“Fabrication and Performances of Microencapsulated *N*-Alkanes with Copolymers Having *N*-Octadecyl Side Chains As Shells”, Industrial & Engineering Chemistry Research, Vol:*53* (4), pp: 678–1687.
5. Salaun F. and Vroman I., 2008,“Influence of Core Materials on Thermal Properties of Melamine Formaldehyde Microcapsules”, European Polymer Journal, Vol:44, pp:849–860.
6. Saihi D., Vroman I., Giraud S. and Bourbigot S., 2006,“Microencapsulation of Ammonium Phosphate with a Polyurethane Shell. Part II. Interfacial Polymerization Technique”, Reactive and Functional Polymers, Vol:66(10**)**, pp: 1118–1125.
7. Saihi D., Vroman I., Giraud S. and Bourbigot S., 2005“Microencapsulation of Ammonium Phosphate with a Polyurethane Shell Part I: Coacervation Technique”,Reactive and Functional Polymers, Vol:64(3), pp:127–138.
8. Giraud S., Bourbigot S., Rochery M., Vroman I., Tighzert L. and Delobel E, 2002,“Microencapsulation of Phosphate: Application to Flame Retarded Coated Cotton”, Polymer Degradation and Stability, Vol:77(2), pp: 285–97.
9. Ai Y., Jin Y., Sun J. and Wei D.Q., 2007,“Microencapsulation of n-Hexadecane as Phase Change Material by Suspension Polymerization”, e-Polymers, Vol: 098, pp:1–9.
10. Alay S., Alkan C. and Göde F, 2012, “Steady-State Thermal Comfort Properties of Fabrics Incorporated with Microencapsulated Phase Change Materials”, Journal of the Textile Institute, Vol:103(7), pp:757-765.
11. Shirin-Abadi A.R., Mahdavian A.R. and Khoee S., 2011,.“New Approach For The Elucidation of PCM Nanocapsules Through Miniemulsion Polymerization with an Acrylic Shell”, Macromolecules, Vol:44, pp:7405–7414.
12. Cho J.S., Kwon A. and Cho C.G., 2002, “Microencapsulation of Octadecane as a Phase-Change Material by Interfacial Polymerization In an Emulsion System”,Colloid and Polymer Science, Vol:280, pp: 260-266.
13. Choi J., Lee J.G., Kim J.H. and Yang H., 2001,“Preparation of Microcapsules Containing Phase Change Materials As Heat Transfer Media By In-Situ Polymerization”,Journal of Industrial and Engineering Chemistry, Vol:**7**, pp:358–362.
14. Onder E., Sarıer N. and Çimen E., 2008, “Encapsulation of Phase Change Materials by Complex Coacervation To Improve Thermal Performances of Woven Fabrics”, Thermochimica Acta, Vol:467(1–2), pp:63–72.
15. Sarıer N. and Önder E., 2007,“The Manufacture of Microencapsulated Phase Change Materials Suitable For The Design of Thermally Enhanced Fabrics”, Thermochimica Acta, Vol:452 (2), pp:149–160.
16. Alkan C., Alay-Aksoy S. and Altun-Anayurt R., 2015,“Synthesis of Poly(Methyl Methacrylate-Co-Acrylic Acid)/N-Eicosane Microcapsules For Thermal Comfort In Textiles”,Textile Research Journal, Vol:85(19), pp:2051–2058.
17. Wang Y., Shi H., Xia T.D., Zhang T. and Feng H.X., 2012, “Fabrication and Performances of Microencapsulated Paraffin Composites with Polymethylmethacrylate Shell Based on Ultraviolet Irradiation-Initiated” Materials Chemistry and Physics**,** Vol: 135(1), pp: 181–187.
18. Alkan C., Sarı A. and Karaipekli A., 2011,“Preparation, Thermal Properties And Thermal Reliability of Microencapsulated N-Eicosane As Novel Phase Change Material For Thermal Energy Storage”, Energy Conversion and Management, Vol:52, pp:687–692.
19. Alkan C., Sarı A., Karaipekli A., Uzun O., 2009,“Preparation, Characterization, And Thermal Properties of Microencapsulated Phase Change Material For Thermal Energy Storage”, Solar Energy Materials & Solar Cells, Vol:93, pp:143–147.
20. Sarı A., Alkan C., Karaipekli A. and Uzun O., 2009,“Microencapsulated N-Octacosane As Phase Change Material For Thermal Energy Storage”, Solar Energy, Vol:83, pp:1757–1763.
21. Sarı A., Alkan C. and Karaipekli A., 2010,“Preparation, Characterization and Thermal Properties of PMMA/N-Heptadecane Microcapsules as Novel Solid–Liquid MicroPCM For Thermal Energy Storage”,Applied Energy, Vol:87, pp:1529–1534.
22. Chang C., Tsai Y., Chiu J. and Chen H., 2009.“Preparation of Phase Change Materials Microcapsules by Using Pmma Network-Silica Hybrid Shell Via Sol–Gel Process”, Journal of Applied Polymer Science, Vol:112**,** pp:1850–1857.
23. Shan X.L., Wang J.P., Zhang X.X. and Wang X.C., 2009,“Formaldehyhe-Free and Thermal Resistant Micropcms Containing N-Octadecane”, Thermochimica Acta,Vol: 494, pp:104–109.
24. Qiu X., Li W., Song G., Chu X. and Tang G., 2012,“Microencapsulated n-octadecane with different methylmethacrylate-based copolymer shells as phase change materials for thermal energy storage”,Energy, 46, p.188–199.
25. Zhang G.H., Bon S.A.F. and Zhao C.Y., 2012,“Synthesis, Characterization and Thermal Properties of Novel Nanoencapsulated Phase Change Materials For Thermal Energy Storage”, Solar Energy, Vol:86(5), pp:1149–1154.
26. Rahman A., Dickinson M.E. and Farid M.M., 2012,“Microencapsulation of a PCM Through Membrane Emulsification And Nanocompression-Based Determination of Microcapsule Strength”, Materials for Renewable and Sustainable Energy, Vol:1(**4**), pp:1-10.
27. Qiu X., Li W., Song G., Chu X. and Tang G., 2012,“Fabrication and Characterization of Microencapsulated N-Octadecane with Different Crosslinked Methylmethacrylate-Based Polymer Shells”, Solar Energy Materials and Solar Cells, Vol:98, pp:283–293.
28. Chen Z.H., Yu F., Zeng X.R. and Zhang Z.G., 2012,“Preparation, Characterization and Thermal Properties of Nanocapsules Containing Phase Change Material *N*-Dodecanol By Miniemulsion Polymerization with Polymerizable Emulsifier”, Applied Energy, Vol:9(1), pp:7–12.
29. Ma Y., Chu X., Li W. and Tang G., 2012,“Preparation and Characterization of Poly(Methyl Methacrylate-*Co*-Divinylbenzene) Microcapsules Containing Phase Change Temperature Adjustable Binary Core Materials”, Solar Energy**,** Vol:86(7), pp:2056–2066.
30. Sarı A., Alkan C., Biçer A., Altuntas A. and Bilgin C., 2014,“Micro/Nanoencapsulated *N*-Nonadecane with Poly(Methyl Methacrylate) Shell For Thermal Energy Storage”, Energy Conversion and Management, Vol:86, pp:614–621.
31. Qiu X., Lu L., Wang J., Tang G. and Song G., 2014,“Preparation And Characterization of Microencapsulated *N*-Octadecane As Phase Change Material With Different *N*-Butyl Methacrylate-Based Copolymer Shells”, Solar Energy Materials and Solar Cells, Vol:128, pp:102–111.
32. Wang Y., Zhang Y., Xia T.D., Zhao W.J. and Yang W.H., 2014,“Effects of Fabricated Technology on Particle Size Distribution and Thermal Properties of Stearic–Eicosanoic Acid/Polymethylmethacrylate Nanocapsules”,Solar Energy Materials and Solar Cells, Vol:(120), pp:481–490.
33. Sarı A., Alkan C. and Özcan A.N., 2015,“Synthesis and Characterization of Micro/Nano Capsules of PMMA/Capric–Stearic Acid Eutectic Mixture For Low Temperature-Thermal Energy Storage In Buildings”, Energy and Buildings, Vol: 90, pp:106–113.

34. Han P., Lu L.,Qiu X., Tang Y. and Wang J., 2015,“Preparation and Characterization of Macrocapsules Containing Microencapsulated PCMS (Phase Change Materials) For Thermal Energy Storage”, Energy, Vol:91, pp:531–539.

35. Al-Shannaq R., Farid M., Al-Muhtaseb S. and Kurdi J., 2015, “Emulsion Stability and Cross-Linking of PMMA Microcapsules Containing Phase Change Materials”, Solar Energy Materials and Solar Cells, Vol:132, pp:311–318.

36. Shi J., Wu X., Fu X. and Sun R., 2015,“Synthesis And Thermal Properties of A Novel Nanoencapsulated Phase Change Material with PMMA and SIO_2 As Hybrid Shell Materials”, Thermochimica Acta, Vol:617, pp:90–94.

37. Alkan C., Altun-Anayurt R. and Alay-Aksoy, S., 2014,“Poly(Methyl Methacrylate-Co-2-Hydroxyethyl Acrylate)/n-Hexadecane Microcapsules as a Reactive Outer Surface Thermal Comfort Additive”, Proceeding of AUTEX 2014 World Textile Conference. Bursa, Turkey.

38. Altun-Anayurt R., Alkan C. and Alay-Aksoy S., 2014,“Poly (Methylmethacrylate-Co-2-Hydroxyethyl Acrylate)/N-Octadecane Microcapsules For Heat Energy Storage”, Proceeding of V. National Polymer Science and Technology Congress. Tokat, Turkey.

39. Konuklu Y., Paksoy H.O. and Unal M., 2015,“Nanoencapsulation of N-Alkanes with Poly(Styrene-Co-Ethylacrylate) Shells For Thermal Energy Storage”, Applied Energy, Vol:150, pp:335–340.

40. Liu X. and Lou Y., 2015,“Preparation of Microencapsulated Phase Change Materials By The Sol-Gel Process And Its Application On Textiles”. Fibres & Textiles in Eastern Europe; Vol:23, 2(110), pp:63-67.