



Synthesis and characterization of poly(methyl methacrylate)/n-hexadecane microcapsules using different cross-linkers and their application to some fabrics

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ABSTRACT

In this study, poly(methyl methacrylate)/n-hexadecane microcapsules were prepared using emulsion polymerization, and their applicability to textiles was studied. Two types of cross-linker, namely allyl methacrylate and ethylene glycol dimethacrylate were used to produce unimodal microcapsule particle size distribution. The characterization of the microcapsules, including particle size and size distribution determination, morphology, and thermal properties was carried out. Mean particle size of microcapsules ranges from 0.22 μm to 1.05 μm . The contents of n-hexadecane in microcapsules are between 29.04% and 61.42% and the melting enthalpies for these ratios are 68.89 J/g and 145.61 J/g, respectively. Prepared microcapsules using ethylene glycol dimethacrylate cross-linker were added to woven fabrics by a conventional pad-cure method to develop textile materials with heat storage property. The enthalpies of microencapsulated PCMs treated fabrics varied between 3.14 J/g and 10.02 J/g for various fabric samples.

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1. Introduction

Phase change materials (PCMs) are thermal energy storage materials that use chemical interactions to store and release heat. Latent heat is stored or released by PCMs as their form change from one state to another. Most commonly solid–liquid PCMs are operated for thermal energy storage applications. When the temperature of a solid liquid PCM increases to its melting point, it absorbs latent heat to breakdown the interactions responsible for the solid state. This stored latent heat releases to surrounding as PCM cools down [1]. Phase change materials have been used to manufacture thermo-regulated textiles for clothing to improve thermal comfort of wearer [2]. They have also been incorporated to textiles for manufacturing of personal heating and cooling devices [3], thermal insulating systems for protective textiles [4], medical textiles, protective textiles [5], household textiles such as blanket, duvets, mattresses, and pillowcase [6].

PCMs are enclosed in thin and resilient polymer shell to form microcapsules of a few micrometers in diameter [1,2]. Microencapsulation is effective method to prevent reaction of PCM with outside environment and their leakage during its liquid phase, to increase heat-transfer area, to provide constant volume [7,8]. Microencap-

sulated phase change materials (microPCMs) which have been widely investigated to manufacture thermo-regulated fibers, fabrics and coatings are powder-like materials [9].

The most widespread PCMs in textile field are paraffin-waxes with various phase change temperatures depending on their carbon numbers. They have been incorporated to textiles due to their high latent heat and they are chemically inert, non-toxic and non-corrosive [1,2,10]. The most preferred paraffin-waxes for textiles are n-eicosane [11,12], n-octadecane [7,8,13–17] and n-hexadecane [7,17–20] and their binary mixtures such as n-eicosane/n-hexadecane [2,8].

The choice of suitable polymer to synthesize microcapsule shell material is linked to the considered application and the required production processes. MicroPCMs used in textile field requires high thermal and mechanical stability that are affected by the shell and core materials. According to the literature survey, microPCMs have yet been synthesized with various natural or synthetic polymers such as gum arabic–gelatin mixture [7], silk fibroin and chitosan [12], melamine–formaldehyde [2,11,13,21,22], poly(urea–formaldehyde) [8], and polystyrene [23] shell materials.

PCMs have been applied to textiles using various manufacturing processes. For example, thermo-regulated fibers were manufactured by filling hollow fibers with PCMs [24–26]. Besides, scientists have tried to produce thermo-regulated fibers by incorporating microPCMs into fiber via melt or wet spinning [27–29]. MicroPCMs were also incorporated into polymer resins to electrospin

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thermo-regulated nanofibers [18,20]. Some researchers have tried to incorporate the microPCMs on the fabrics by means of pad dry cure method [2,11] or coating [7,13–15,30,31]. Moreover microPCMs have been applied in the fabrication of heat-insulated polyurethane foams [9,32–34].

As can be seen from the literature survey, there is no investigation reported on preparation of microPCMs with PMMA shell and incorporation of them to the fabrics. Therefore we aimed to produce PMMA/n-hexadecane microcapsules with suitable particle sizes and thermal properties for application to the fabrics. For this reason, n-hexadecane was chosen as core material because it has a suitable melting point of 18.2 °C. PMMA/n-hexadecane microcapsules with poly(methyl methacrylate) (PMMA) shell and n-hexadecane core were prepared by emulsion polymerization method. To produce unimodal particle size distribution; allyl methacrylate, and ethylene glycol dimethacrylate were used as cross-linkers. The particle size and its distribution, structure, and thermal properties of PMMA/n-hexadecane microcapsules were investigated. PMMA/n-hexadecane microcapsules prepared by using ethylene glycol dimethacrylate were applied to the cotton, cotton/polyester, and polyester fabrics.

2. Experimental

2.1. Material

n-Hexadecane (Fluka) was used as received. Methyl methacrylate, allyl methacrylate, and ethylene glycol dimethacrylate were obtained from Sigma Aldrich Company and they were doubled distilled before use. Triton X100 (Merck) and tert butylhydroperoxide (Merck) were used as surfactant and initiator respectively. Ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), and sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_7$) were all obtained from Sigma Aldrich and used without further purification.

In this study, microencapsulated PCMs were applied to scoured and bleached woven fabrics to produce thermo-regulated fabrics. The fabrics were 100% cotton with a weight of 108 g/m², 50/50 cotton/polyester blend with a weight of 110 g/m², and 100% microfiber polyester with a weight of 118 g/m². The blend fabric has 46 yarns per cm in warp direction and 25 yarns per cm in weft direction while the warp and weft yarn densities of cotton and microfiber polyester fabrics are 60 warps/cm and 35 weft/cm, respectively. Polyurethane (Baypret from Bayer) was used as cross-linker to fix the microcapsules to the fabrics.

2.2. Preparation of PMMA/n-hexadecane microcapsules

PMMA microcapsules were prepared by using oil-in-water emulsion polymerization process applied by Alkan et al. [34]. In the first step, a total 94 mL distilled water, 25 g n-hexadecane, and 1 g of Triton X-100 (surfactant) were mixed at room temperature to prepare mixture. This mixture was prepared at room temperature because n-hexadecane was liquid phase at this temperature. In the second step, total 25 g monomer, 2.5 g cross-linker, 1 mL freshly prepared $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution (prepared by mixing 0.3 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with 200 mL distilled water) and 0.25 g ammonium persulphate were added to this mixture. The resultant mixture was stirred to form emulsion at 2000 rpm for 30 min by mechanical stirrer. Therefore oil-in-water emulsion system was prepared. Addition of a second initiator can be used to produce uniformly sized and shaped microcapsules. So an extra of 0.25 g $\text{Na}_2\text{S}_2\text{O}_3$ and 1.00 g 70% tert butylhydroperoxide solution were added at this point and the reaction medium was heated to 90 °C under nitrogen atmosphere. During reaction, the resultant mixture was stirred at 1000 rpm. The stirring time of 3.5 and 5 h were used to pre-

Table 1
Microcapsule application conditions to the fabrics.

Microcapsule	Fabric code	Microcapsule concentration (g/L)	PU concentration (g/L)	Fixation conditions
PMMA/n-hexadecane/ethylene glycol dimethacrylate	CO1	6	30	100 °C, 5 min
	CO2	50	100	160 °C, 3 min
	CO/PES	50	100	160 °C, 3 min
	Microfiber PES	50	100	160 °C, 3 min

pare PMMA/n-hexadecane microcapsules by using ethylene glycol dimethacrylate and allyl methacrylate cross-linkers, respectively. In the end of reaction duration, the liquid part of the emulsion system was decanted to isolate residual hexadecane and emulsifier. The emulsion was washed several times and dried at 40 °C to evaporate the water [20].

2.3. Characterization of PMMA/n-hexadecane microcapsules

The morphology of the PMMA/n-hexadecane microcapsules was investigated using scanning electron microscope (SEM, LEO 440 Computer Controlled Digital). The SEM images with several magnifications between 2000× and 30k× were used. The surface of the microcapsules was coated with gold to supply surface conductivity during SEM analysis. The particle size of microcapsules was measured using Lucia 32 G image analysis program. More than 400 microcapsules were recorded. The particle size distribution was also determined using SSPSS 10.0 for Windows.

Thermal properties of microencapsulated PCMs were determined using differential scanning calorimeter (DSC, Perkin-Elmer Jade) at the heating and cooling rate of 5 °C/min between the 0 °C and 50 °C under a constant stream of nitrogen at a flow rate of 60 mL/min. The average 5 mg of samples weight was used. The percentage of encapsulated n-hexadecane in PMMA polymer were calculated by Eq. (1),

$$\text{PCM}(\text{wt}\%) = \frac{\Delta H_{\text{microPMMA}}}{\Delta H_{\text{PCM}}} \times 100 \quad (1)$$

where PCM (wt%) represents the percentage of n-hexadecane in the PMMA microcapsules, while $\Delta H_{\text{microPMMA}}$ and ΔH_{PCM} represent enthalpies of microcapsules and n-hexadecane, respectively.

The spectroscopic analyses of the PMMA/n-hexadecane microcapsules were performed on KBr disks using an FT-IR instrument (Jasco 430 model FT-IR spectrophotometer). The number of scan was 16 and resolution was as 4 cm⁻¹ during FT-IR analysis.

2.4. Application of the microcapsules to the fabrics

The dried PMMA/n-hexadecane microcapsule powders prepared using ethylene glycol dimethacrylate cross-linker were mixed with a polyurethane binder (PU) solution in distilled water. The cotton (CO), cotton/polyester blends (CO/PES) and microfiber polyester (PES) fabrics were impregnated into this solution under the conditions of 2 bar pressure and 2 rpm rotating speed using foulard. Then fabrics were cured using dryer. The conditions of curing and the concentration of microcapsule were given in Table 1 [35].

The fabrics containing microcapsules were washed at 40 °C for 30 min according to the TS EN 20105-C06: 2001; A2S.

2.5. Evaluation of the fabrics treated with microcapsules

The heat storage capacity and phase change temperatures of the microcapsule-treated fabrics were determined by a DSC instrument. The analysis conditions used to measure thermal properties of microcapsules were also used in measuring the thermal properties of fabrics.

The surface of the fabric was coated by gold and then analyzed using a SEM instrument (Phillips XL-30S FEG).

3. Results and discussion

Characterization of microencapsulated materials can be overcome using different kinds of sophisticated techniques. In general electron microscopy plays the major role because it can show if the produced material is microcapsules or not easily. Also particle size and its distribution can be effectively determined using electron microscopy technique. Because the material properties are mainly dependent on the structure and constitution, the analysis of constitution and chemical structure is secondarily important. The next one for characterization of the microencapsulated species changes upon the target properties and applications. Because the microencapsulated PCMs are produced for energy storage and thermal comfort, the characterization is comprised of thermal analysis.

3.1. The morphology and microencapsulated PCMs

For primary characterization of microencapsulated PCMs, physical structure, particle diameter and particle size distribution of the micro particles are very important for their properties and applicability. Particle shape, size and size distribution of the particles were all evaluated from the images taken from electron microscopy at several magnifications.

SEM images of the PMMA/n-hexadecane microcapsules produced by using allyl methacrylate as cross-linker at different magnifications were given in Fig. 1. The PMMA/n-hexadecane microcapsules have complex morphology, characterized by micro sized beads with partially rough outer surface or clusters. They have relatively uniform sizes but not uniform spherical shape. It may be advantageous of high heat transfer ratio and applicability due to extended surface area.

The particle size distribution of PMMA/n-hexadecane microcapsules prepared using allyl methacrylate as cross-linker was presented in Fig. 2. The size distribution appears as homogenous and the particle size intensively ranges from 0.63 μm to 1.63 μm . The particles have a mean particle size of 1.05 μm with relatively narrow size distribution.

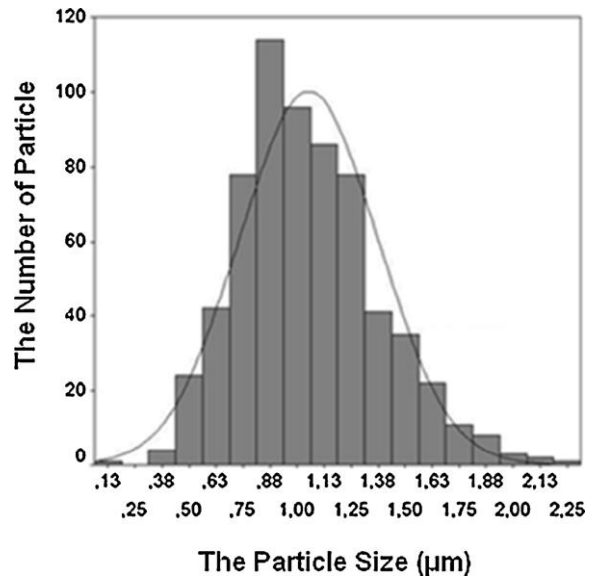


Fig. 2. The PSD of PMMA/n-hexadecane microcapsules produced by using allyl methacrylate.

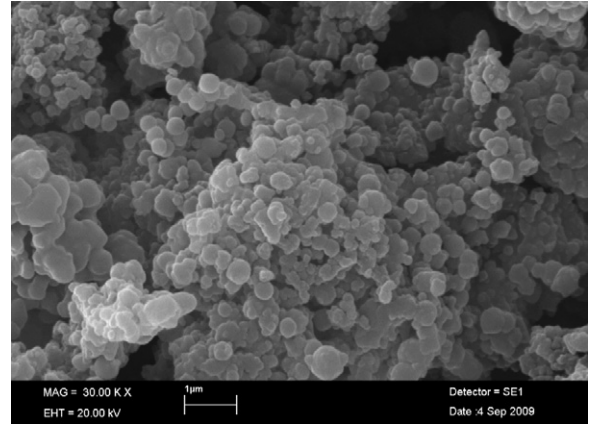


Fig. 3. SEM images of PMMA/n-hexadecane microcapsules produced by using ethylene glycol dimethacrylate.

The SEM images of PMMA/n-hexadecane microcapsules produced by using ethylene glycol dimethacrylate as cross-linker were shown in Fig. 3. The PMMA microcapsules have almost spherical shape and smoother surface here.

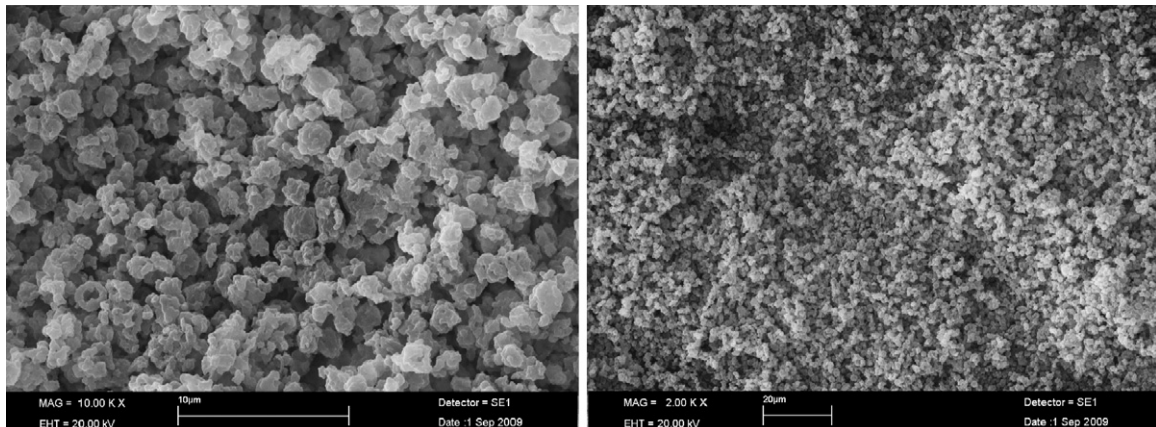


Fig. 1. SEM images of PMMA/n-hexadecane microcapsules produced by using allyl methacrylate.

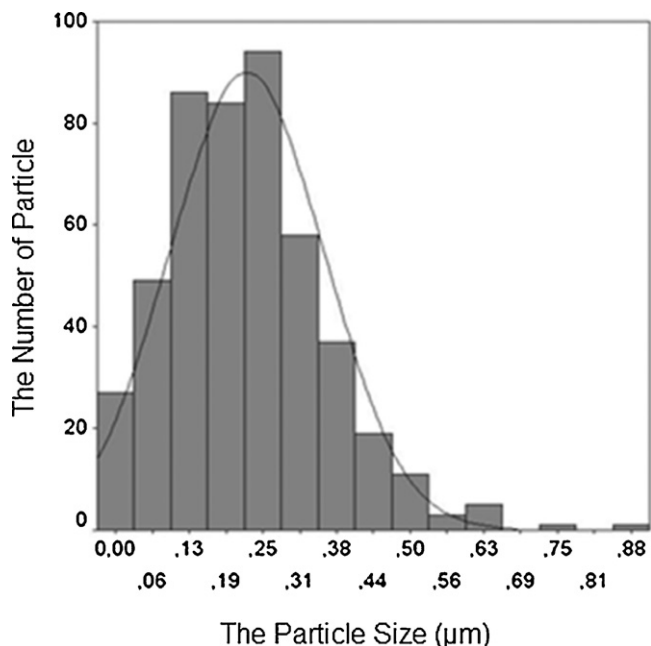


Fig. 4. The PSD of PMMA/n-hexadecane microcapsules produced by ethylene glycol dimethacrylate.

Fig. 4 represents the particle size distribution of PMMA/n-hexadecane microcapsules prepared using ethylene glycol dimethacrylate as cross-linker. The particle size of microcapsules varied from 0.06 µm to 0.88 µm, exhibiting a very narrow distribution and the mean particle size of the microcapsules is 0.22 µm. It is clear that the particle size of microcapsules decreases and nano-size microcapsules are produced when ethylene glycol dimethacrylate is used. PMMA/n-hexadecane microcapsules produced using ethylene glycol dimethacrylate can be called as nanocapsules.

3.2. The spectroscopic analyses of microcapsules

Generally FT-IR spectroscopy is used to characterize the microcapsules structurally [7,22,34] because it is possible to prove the existence of materials in the microcapsules by FT-IR spectroscopy. In this work, FT-IR spectra of the n-hexadecane, microPCMs and MMA were given in Fig. 5 to prove the co-presence of methyl methacrylate (MMA) and n-hexadecane in the microcapsules. In the pure n-hexadecane spectra, the peaks at 2956 and 2916, and 2848 cm⁻¹ represents the symmetrical stretching vibration of -CH₃ and -CH₂ group, respectively. The peaks at 1471, 1461, 1377 cm⁻¹ belong to the deformation vibration of -CH₂ and -CH₃ groups. The peak at 729 cm⁻¹ represents the rocking vibration of -CH₂ group and it present in the spectra of microcapsules while it is not available in MMA spectra. This revealed the presence of n-hexadecane in the structure of microcapsules. In the n-hexadecane/PMMA spectrum, the C-H stretching peaks of MMA are overlapped with the peaks of paraffin as the peak at 1730 cm⁻¹ shows carbonyl groups of MMA. The peak at 1440 cm⁻¹ is due to C-H bending and the peaks at 1200 cm⁻¹ can be assigned to the C-O stretching of the ester group [34]. Consequently, FT-IR spectra of PMMA/n-hexadecane microcapsules, methyl methacrylate and n-hexadecane revealed the coexistence of n-hexadecane and MMA in the microcapsules. The slight differences in FT-IR spectra of microencapsulated particles are due to the difference of cross-linkers used. They are not distributive because the use of cross-linker in the synthesis is only 2% at most.

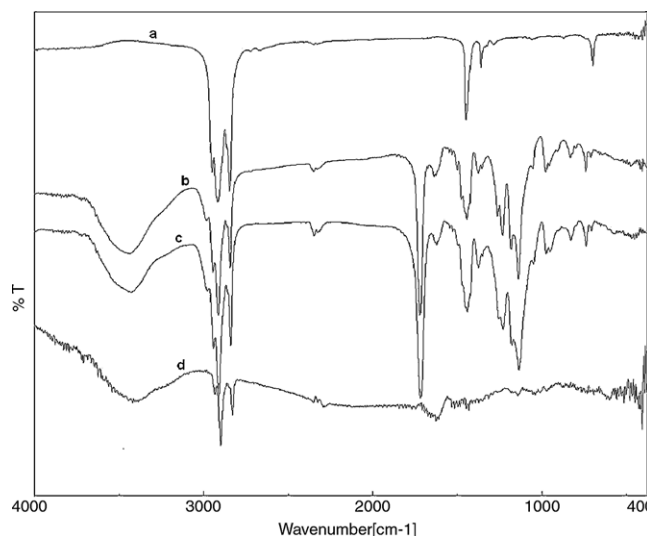


Fig. 5. FT-IR spectra for (a) n-hexadecane, (b) PMMA/n-hexadecane microcapsules with allyl methacrylate cross-linker, (c) PMMA/n-hexadecane microcapsules with ethylene glycol dimethacrylate cross-linker, and (d) MMA.

3.3. Thermal properties of microcapsules

Thermal energy storage capacity of the PMMA/n-hexadecane microcapsules prepared using allyl methacrylate and ethylene glycol dimethacrylate were investigated using DSC and their curves were shown in Figs. 6 and 7. It is seen from Fig. 6 that PMMA/n-hexadecane microcapsules prepared by allyl methacrylate melt at 15.69 °C, and crystallize at 13.19 °C as pure n-hexadecane [1] melts at 18.2 °C, and crystallizes at 16.2 °C. The phase change temperatures of n-hexadecane decreases slightly in the microcapsules. The latent heat of melting and freezing of microcapsules were measured as 68.89 J/g and -50.31 J/g, respectively. The percentage of encapsulation of n-hexadecane by PMMA was calculated as 29.04%. The thermal properties of the PMMA/n-hexadecane microcapsules prepared by using ethylene glycol dimethacrylate were displayed in Fig. 7. Microcapsules melt at 17.34 °C, and crystallize at 14.85 °C which is also slightly lower than pure n-hexadecane. The decrease in the phase change temperature of n-hexadecane is lower in the microcapsules with ethylene glycol dimethacrylate cross-linker. The latent heat of melting and freezing of PMMA/n-hexadecane microcapsules with allyl methacrylate are 145.61 J/g and -128.19 J/g, respectively. The percentage of n-hexadecane in PMMA microcapsules synthesized by using ethylene glycol dimethacrylate was calculated as 61.42%. As a result it is clear that the type of crosslinker is effective on the thermal energy storage properties of PMMA/n-hexadecane microcapsules.

Thermal stability of microcapsules against to high temperatures applied during thermal fixation of microcapsules to the fabrics was also investigated. For this aim, PMMA/n-hexadecane microcapsules prepared by ethylene glycol dimethacrylate were treated at 150 °C, for 10 min. Fig. 8 displays the DSC curve of PMMA microcapsules after heat treatment. DSC data indicates that there is no significant decrease in the melting and crystallization temperature of the heat treated microcapsules. The latent heat for melting decreases from 145.61 J/g to 136.23 J/g and it can be thought the microcapsules are suitable for textile treatments even at high temperatures.

3.4. Thermal properties of the fabrics treated with microcapsules

PMMA/n-hexadecane microcapsules prepared by ethylene glycol dimethacrylate were applied to the fabrics because of their higher enthalpy and smaller particle sizes. Microcapsules were

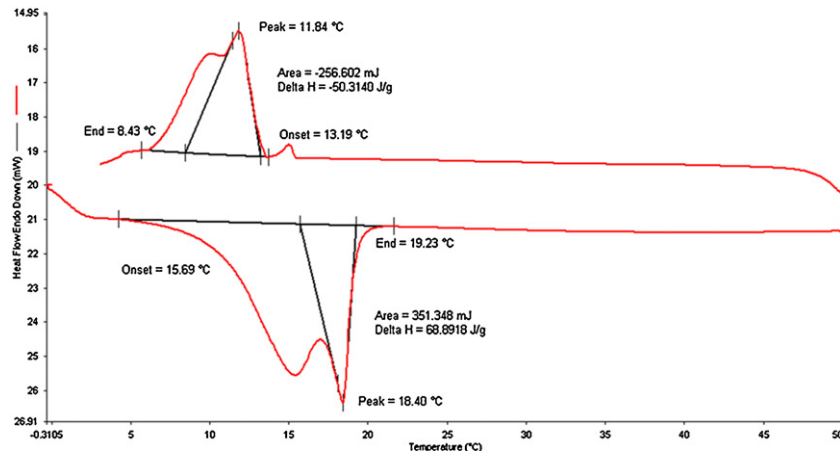


Fig. 6. DSC curve of PMMA/n-hexadecane microcapsules prepared by allyl methacrylate.

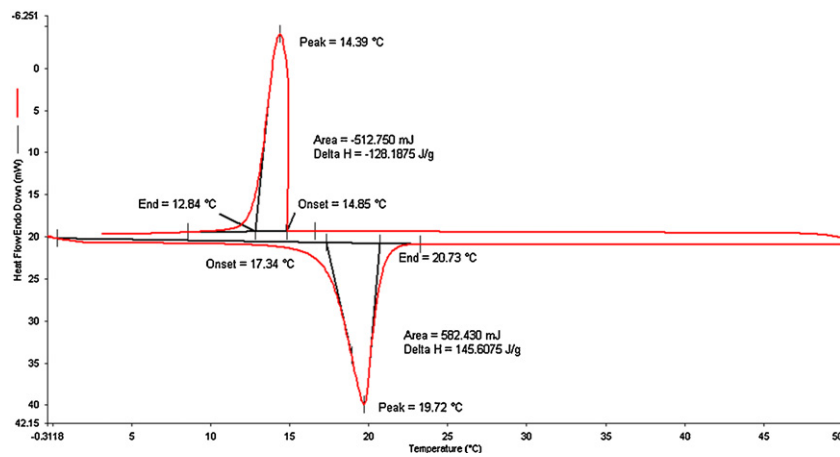


Fig. 7. DSC curve of PMMA/n-hexadecane microcapsules prepared by ethylene glycol dimethacrylate.

applied to various fabrics at application conditions given in Table 1. The thermal properties of these fabrics with microcapsules were investigated by DSC analysis. DSC curves of the fabrics were given in the Fig. 9. The melting (T_m) and crystallization (T_c) temperatures, the latent heats of melting (ΔH_m) and crystallization (ΔH_c) of the fabric samples obtained from DSC analysis were summarized in Table 2. DSC results showed that microcapsules were consistent in fabrics after treatment and the heat stored by the fabrics

was considerably high when the results were compared to the findings from various other studies [11,13,15]. Phase change temperatures measured for the fabrics were almost the same as that of the microcapsules showing that fabrics do not create any more shell effect. As the microcapsule concentration added on the same cotton fabric sample increases from 6 g/L to 50 g/L, the heat storage capacity of the treated fabric slightly increases from 3.14 J/g to 4.95 J/g. The latent heat storage capacity of the thermo-regulated

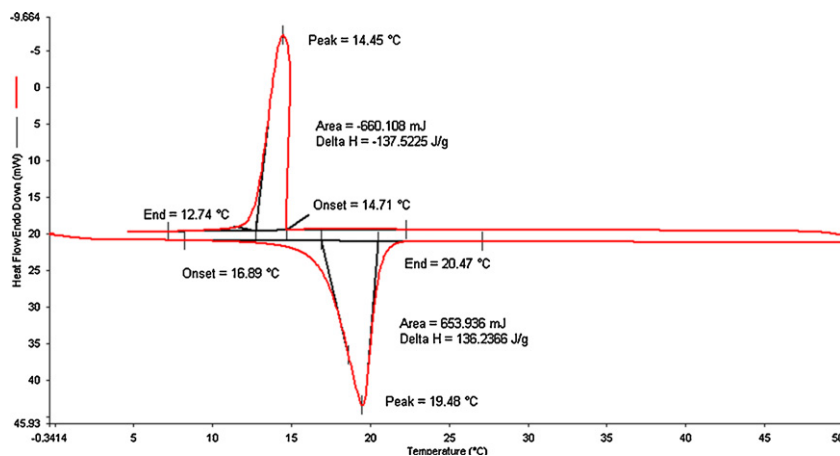


Fig. 8. DSC curve of PMMA/n-hexadecane microcapsules prepared by ethylene glycol dimethacrylate after heat treatment.

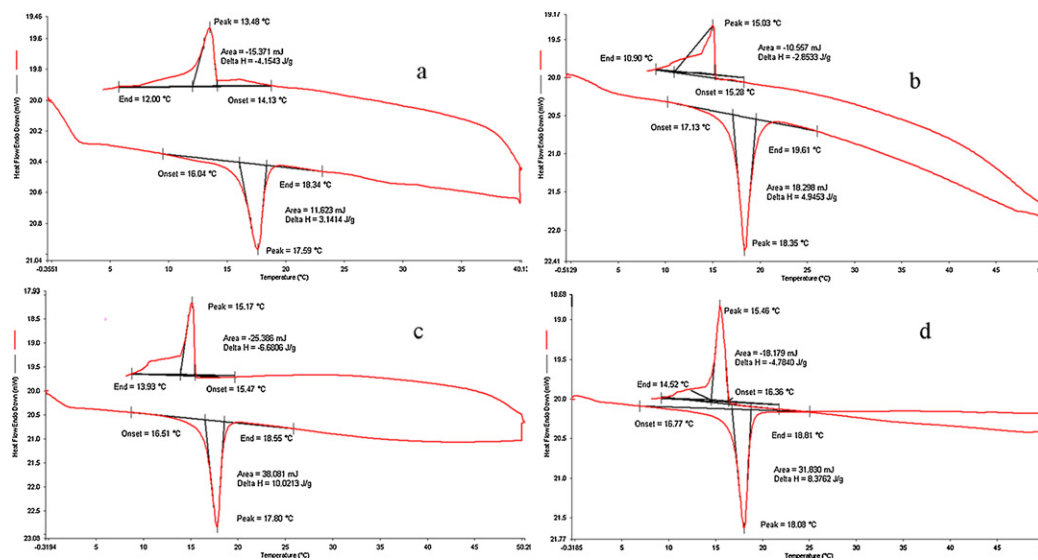


Fig. 9. DSC curves for (a) CO1, (b) CO2, (c) CO/PES, and (d) microfiber/PES fabrics.

Table 2

Thermal properties of the fabrics treated with PMMA/n-hexadecane microcapsules.

The fabric code	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)
CO1	16.04	14.13	3.14	-4.15
CO2	17.13	15.28	4.95	-2.85
CO/PES	16.51	15.47	10.02	-6.68
Microfiber PES	16.77	16.36	8.38	-4.78

fabrics depends on the amount of the microcapsules added on the fabric and the amount of the microcapsules added on the fabric is related with the ratio of binder/microPCMs composite impregnated to the fabric. The latent heat of the composite decreases as the binder/microPCMs ratio increases [2]. The binder/microPCM ratio applied to the CO1 fabric (30/6) is higher than that of CO2 fabric (100/50). Therefore the latent heat stored by CO1 fabric can be lower than that of CO2 fabric.

CO2, CO/PES, and microfiber PES fabrics had different heat storage capacities although the same concentration of microcapsule (50 g/L) was added. The CO/PES blend fabric was capable of absorbing 10.02 J/g of heat while CO2 and microfiber polyester fabrics were able to store 4.95 J/g and 8.38 J/g of the latent heat respectively. The difference among the latent heat capacity result from binary effect of fabric density and fabric raw material. When the fabric construction has enough pore that microcapsules can be

placed into, heat storage capacity of the fabric increases. Cotton and microfiber polyester fabrics have tight structure because of high fabric density so their heat capacities are lower than blend fabric having more porous. On the other hand microfiber polyester fabric more surface area than blend fabric that microcapsules can be hold on to fabric because of micro fiber size. The fabric raw material also influences the heat storage capacity of the microcapsule treated fabrics. Polyester is more compatible with acrylic microcapsules than cotton due to structural similarity. Adhesion between the two materials increases depending on similarity of their dispersive and non-dispersive groups (polar groups) [36]. Since both polyesters and acrylic polymers have ester bonds as polar groups at the backbone and at the pendant group, respectively. Therefore the fabrics made from polyester fiber can be more attractive material for acrylic microcapsules due to ester constitution in both. Moreover polar OH groups present in the cellulosic cotton make it more hydrophilic as the microcapsules are hydrophobic.

3.5. The morphology of the microcapsule-treated fabrics

Cotton fabric with minimum heat storage capacity and cotton/polyester fabric with maximum heat storage capacity were chosen to investigate the fabric morphology. SEM images of the cotton fabric given in Fig. 10 shows that microcapsules were distributed on the surface of fibers homogeneously. Microcapsules

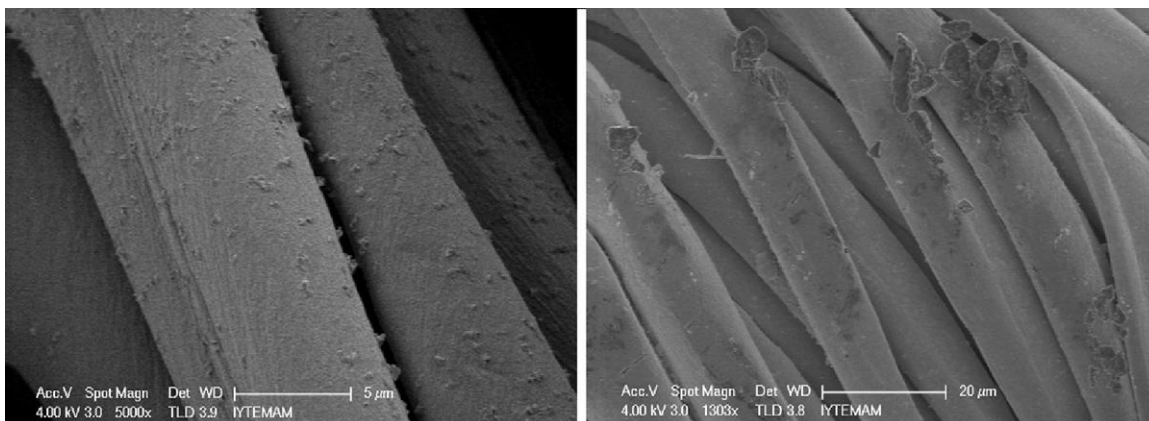


Fig. 10. SEM images of cotton fabric treated with microcapsules before (left) and after once laundering (right).

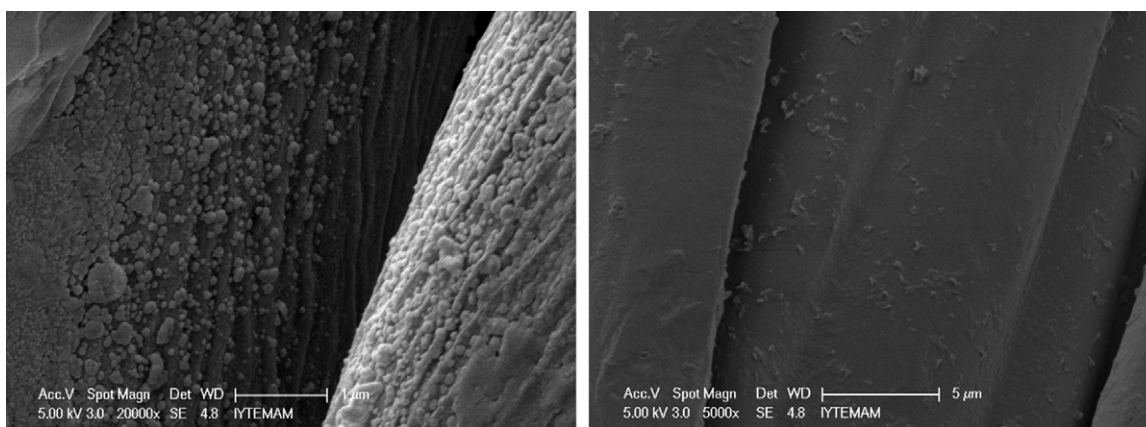


Fig. 11. SEM images of cotton/polyester blend fabric treated with microcapsules before (left) and after once laundering (right).

were incorporated on the fibers without modifying the fabric surface. There was no binder residual coated on the fiber surface and on the microcapsules. It could be thought that microcapsules were linked to the fiber surface by creating cross-linking. Fig. 10 indicated that after once laundering, microcapsules were present on the fabric surface. Also after laundering destroyed polyurethane remnant used to fix microcapsules on the fabric were seen on the surface.

Fig. 11 shows the SEM images of the cotton/polyester blend fabrics surface before and after laundering, respectively. The settlement of the microcapsules on the surface of the blend fabric was similar to that of cotton fabric surface. Microcapsules were distributed on the surface of fibers intensively. There were more microcapsules on the fabric surface that was not laundered compared to laundered fabric.

4. Conclusions

PMMA/n-hexadecane microcapsules containing n-hexadecane as core material were produced by emulsion polymerization method. Two types of cross-linker, namely allyl methacrylate and ethylene glycol dimethacrylate were used to produce unimodal microcapsule particle size. The data obtained from SEM analysis indicated that the mean particle size PMMA/n-hexadecane microcapsules were ranged from 0.22 μm to 1.05 μm , exhibiting a narrow distribution. Microcapsules had almost a unimodal size distribution and spherical shape. The particle size and structure of microcapsules changed depending upon the cross-linker type. PMMA/n-hexadecane microcapsules prepared by using ethylene glycol dimethacrylate were nano-sized particles and had more spherical surface. The n-hexadecane presence in the microcapsules was proved by FT-IR spectroscopy analysis.

The phase change temperatures of the PMMA/n-hexadecane microcapsules prepared by ethylene glycol dimethacrylate cross-linker were very close to that of n-hexadecane. Microcapsules prepared by allyl methacrylate had lower phase change temperatures than that of n-hexadecane. Two types of PMMA/n-hexadecane microcapsules had considerably high enthalpy to be enough for textile applications. PMMA/n-hexadecane microcapsules prepared by ethylene glycol dimethacrylate had higher heat capacity. It was also concluded that cross-linker type affect thermal properties of microcapsules.

The PMMA/n-hexadecane microcapsules were incorporated to several fabrics by pad-cure method. The cotton, cotton/polyester, and microfibre polyester fabrics treated with microcapsules at the same concentration were capable of heat absorbing 4.95 J/g, 10.02 J/g, and 8.38 J/g, respectively. The fabric constitution affected the heat storage capacity of the microcapsules incorporated fabrics

due to the chemical compatibility of the fabric material and shell material of microcapsules.

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