Synthesis and Thermal Properties of Poly(*n*-butyl acrylate)/*n*-Hexadecane Microcapsules Using Different Cross-Linkers and Their Application to Textile Fabrics

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ABSTRACT: This study focused on the preparation, characterization, and determination of thermal properties of microencapsulated *n*-hexadecane with poly(butyl acrylate) (PBA) to be used in textiles with heat storage property. Microcapsules were synthesized by emulsion polymerization method, and the particle size, particle size distribution, shape, and thermal storage/release properties of the synthesized microcapsules were analyzed using Fourier-transform infrared spectroscopy, scanning electron microscopy, and differential scanning calorimetry techniques. Allyl methacrylate, ethylene glycol dimethacrylate, and glycidyl methacrylate were used as cross-linkers to produce unimodal particle size distribution. MicroPBA microcapsules produced using allyl methacrylate cross-linker were applied to 100% cotton and 50/50% cotton/polyester blend fabrics by pad-cure method. The mean particle size of microcapsules ranges from 0.47 to 4.25 μm. Differential scanning calorimetry analysis indicated that hexadecane in the microcapsules melts at nearly 17°C and crystallizes at around 15°C. The contents of *n*-hexadecane of different PBA microcapsules were in the range of 27.7–50.7%, and the melting enthalpies for these ratios were between 65.67 and 120.16 J/g, respectively. The particle size and thermal properties of microcapsules changed depending on the cross-linker type. The cotton and 50/50% cotton/polyester blend fabrics stored 6.56 and 28.59 J/g thermal energy, respectively. The results indicated that PBA microcapsules have the potential to be used as a solid-state thermal energy storage material in fabrics. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2821–2829, 2011

Key words: thermal comfort; poly(*n*-butyl acrylate); *n*-hexadecane; microencapsulation

INTRODUCTION

Phase change materials (PCMs) are widely used for thermal conditioning in buildings and thermoregulating in textiles because of the latent heat energy storage and release during phase change. Considerable amount of thermal energy is transferred on phase change process.[1] The technology of PCMs based on the concept of incorporating the encapsulated PCMs into the textile structures in clothing has been developed for the purpose of improving thermoregulating property of textiles.[2]

PCMs give thermal insulation property to textiles and develop thermal comfort of clothing. PCM-incorporated textiles offer temporary thermal insulation during phase changing process by storing and releasing the latent heat. This temporary thermal insulation is called dynamic thermal insulation and terminates when the phase change of the PCM is completed. Keeping the body temperature constant is important to provide thermal comfort and also to prevent fatal health problems caused by abrupt changes in body temperature.[3–5]

Mostly paraffins with various phase change temperatures depending on carbon numbers have been preferred in textile industry. The preferred paraffins to produce microencapsulated PCMs (microPCMs) for textiles are *n*-heptadecane, *n*-octadecane, *n*-nonadecane, *n*-hexadecane, and *n*-eicosane.

To prevent the liquid hydrocarbons from migrating within a fibrous substrate, they need to be microencapsulated.[2,3] The advantages of microencapsulated paraffin wax are reduction in the reactivity of the paraffin with the outside environment, increase in the heat transfer area, and permission of the core material to withstand frequent changes in volume of the storage material as the phase change occurs.[6]

Microencapsulated PCM is composed of PCM as core and a protective polymer shell to maintain the

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shape and prevent leakage of PCM during the phase change process.[6] Zou et al.[7] synthesized microPCMs with hexadecane core and polyurea shell to be applied to textile fibers using interfacial polycondensation method. In addition, Kim and Cho[8] used polyurea/octadecane microcapsules to produce fabrics with heat storage property. Moreover, Choi et al.[9] synthesized melamine formaldehyde microcapsules with octadecane core to be used for polyester fabric. However, recently Arabic gum, chitosan, gelatin, etc. are investigated as capsule shell material because melamine formaldehyde and urea formaldehyde resins causes environmental and health problems. Deveci and Basal[10] used silk fibroin and chitosan polymers to prepare microcapsules containing eicosane that melts at temperature near skin temperature. In another study, Önder et al.[11] prepared microPCMs with gum Arabic and gelatin polymer shell and octadecane, hexadecane, and nonadecane core materials using complex coacervation method.

The key parameters of microencapsulated PCMs are phase change temperature range, heat storage/release capacity, particle size and its uniformity, PCM content, thermal and chemical stability, stability to mechanical action, and heat conductivity. Diameters of microPCMs can range from 1 to 1000 μm. Microcapsules with particle size in the range of 0.5–10 μm are used for incorporation to textile fibers. MicroPCM particles with particle size between 10 and 100 μm can be incorporated to foams or fabric coatings.[2,5]

PCMs can be incorporated into spinning polymer solutions or melts during fiber spinning[12–18,20] or can be applied to the fabrics by finishing processes such as conventional pad-dry-cure method or coating.[9,21,22]

In this study, microPCMs were prepared through an emulsion polymerization of poly(butyl acrylate) (PBA) as a shell and *n*-hexadecane as a core. Three different cross-linkers, namely allyl methacrylate, ethylene glycol dimethacrylate, and glycidyl methacrylate, were used to observe the formation of microcapsules and the effect of cross-linkers on the thermal properties of the microcapsules. The prepared microcapsules were used for producing fabrics with heat storage properties. The microcapsules-applied fabrics were preliminarily tested for their thermal energy storage property. The morphologies, particle size distribution, structures, and thermal properties of microPBA microcapsules were characterized by scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectroscopy, and differential scanning calorimetry (DSC) techniques, respectively. Prepared microcapsules were added to cotton and cotton/polyester blend fabrics by pad-cure process to develop thermoregulating fabrics.

TABLE I
Fabric Construction and Properties

Material	Construction	Warp density (yarn/cm)	Weft density (yarn/cm)	Weight (g/m^2)
100% Cotton	Weaving	60	35	108
50/50% Cotton/polyester	Weaving	46	25	110

EXPERIMENTAL

Materials

n-Hexadecane (Fluka, Switzerland) was of analytical grade and used as received. *n*-Butyl acrylate, allyl methacrylate, ethylene glycol dimethacrylate, and glycidyl methacrylate (Sigma Aldrich, USA) were all double distilled before use. Triton X-100 (Merck) and tertbutyl hydroperoxide (Merck, Germany) were used as received. Ferrous sulfate heptahydrate, ammonium persulfate, and sodium thiosulfate (all from Sigma Aldrich) were also of analytical grade and used without further purification.

The fabrics were scoured and bleached 100% cotton fabric and 50/50% cotton/polyester blend. The fabric construction and properties are given in Table I. To fix the microcapsules to the fabric polyurethane binder (Baypret from Bayer) was used.

Preparation of microPBA microcapsules

MicroPBA microcapsules were prepared using emulsion polymerization method. The procedure applied by Alkan et al.[6] in the synthesis of poly(methyl methacrylate)/paraffin microcapsules for solar space heating–cooling applications is used. *n*-Butyl acrylate monomer and *n*-hexadecane were assembled as oil phase. A total of 94 mL deionized water, 25 g hexadecane, and 1 g of Triton X-100 (surfactant) were mixed at room temperature. A total of 25 g *n*-butyl acrylate monomer, 2.5 g cross-linker, 1 mL freshly prepared $FeSO_4{\cdot}7H_2O$ solution (prepared by dissolving 0.3 g $FeSO_4{\cdot}7H_2O$ in 200 mL distilled water), and 0.25 g ammonium persulfate were added. The resultant mixture was stirred to form uniformly distributed emulsion at 2000 rpm for 30 min. Addition of a second initiator can produce uniformly sized and shaped microcapsules. Thus, an extra of 0.25 g $Na_2S_2O_3$ and 1.00 g 70% tertbutyl hydroperoxide solution were added at this point, and the reaction medium was heated to 90°C under nitrogen atmosphere. At this temperature, the resultant mixture was stirred at 1000 rpm for an average of 4 hr. Most of the emulsion coagulated, and 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

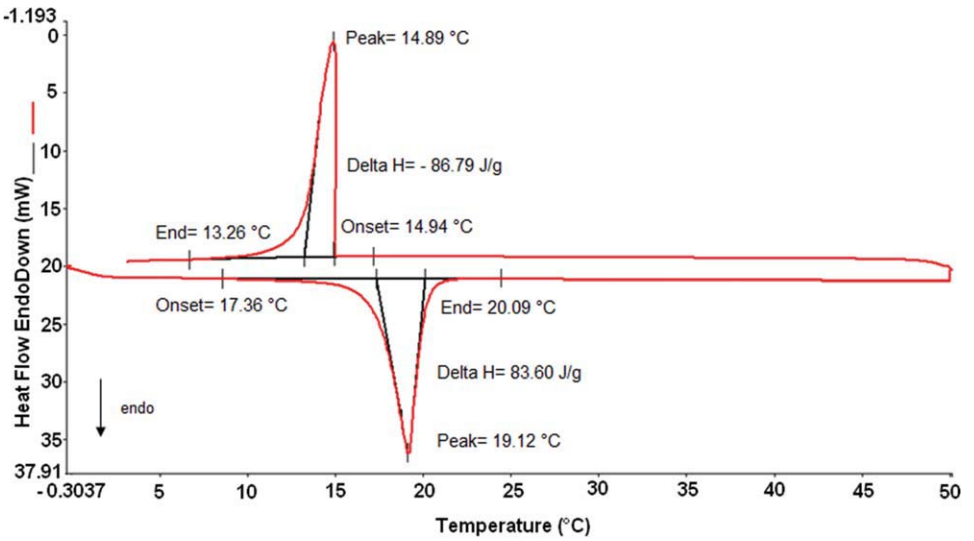

Figure 1 DSC curve of microPBA1 microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the water.[23] The microcapsules were obtained at high yield by each of the cross-linkers.

MicroPBA microcapsules prepared using allyl methacrylate, ethylene glycol dimethacrylate, and glycidyl methacrylate as cross-linkers were represented as microPBA1, microPBA2, and microPBA3, respectively.

Characterization of the microcapsules

The morphology of the microcapsules was investigated using a SEM instrument (LEO 440 Computer Controlled Digital). The particle size of microcapsules was measured using Lucia 32 G Version 4.11 image analysis program.[23]

The thermal properties of microPBA microcapsules and fabrics-incorporated microcapsules such as melting and crystallization temperatures and latent heat were determined by DSC (Perkin–Elmer Jade DSC). The analyses were carried out at 5°C/min heating rate under a constant stream of argon at flow rate of 60 mL/min. Also, encapsulation ratio of *n*-hexadecane in PBA shell was calculated by eq. (1),

$$\mathrm{PCM(wt\%)} = \frac{\Delta H_{\mathrm{microPBA}}}{\Delta H_{\mathrm{PCM}}} \times 100$$

where PCM(wt %) represents the content of *n*-hexadecane in the microcapsules, whereas $\Delta H_{\mathrm{microPBA}}$ and ΔH_{PCM} represent phase change enthalpies of *n*-hexadecane in microcapsules and pure *n*-hexadecane, respectively.[23]

The spectroscopic analyses of the microcapsules were performed on KBr disks using a FT-IR instrument. FT-IR spectra of *n*-hexadecane, *n*-butyl acrylate, and microencapsulated PCMs were obtained using a Jasco 430 model FT-IR spectrophotometer.[23]

Application of the microcapsules to the fabrics

To produce the fabric with heat storage property, microPBA1 microcapsules were added on the fabrics. All microcapsules are PBA shell capsules, and the interaction between the binder and the capsules were expected to be the same. Thus, microPBA1 was chosen as representative example.

MicroPBA1 microcapsules were mixed with a 100 g/L polyurethane binder solution in distilled water. The fabric samples were impregnated into this solution under the conditions of 2 bar pressure and 2 rpm rotating speed using foulard. Then, the fabrics were cured at 160°C for 3 min. The concentration of the microcapsules was adjusted to 50 g/L in the solution.[23]

Evaluation of the treated fabrics

The heat storage capacity and phase change temperatures of the microcapsule-treated fabrics were measured using the DSC instrument under the same conditions with microcapsules.[23]

RESULTS AND DISCUSSION

Thermal properties of the microcapsules

The thermal properties of microPCMs are affected by the encapsulated ratio and the phase changing temperature, which can be determined by means of DSC analysis. DSC curves of microPBA1, microPBA2, and microPBA3 microcapsules are shown in

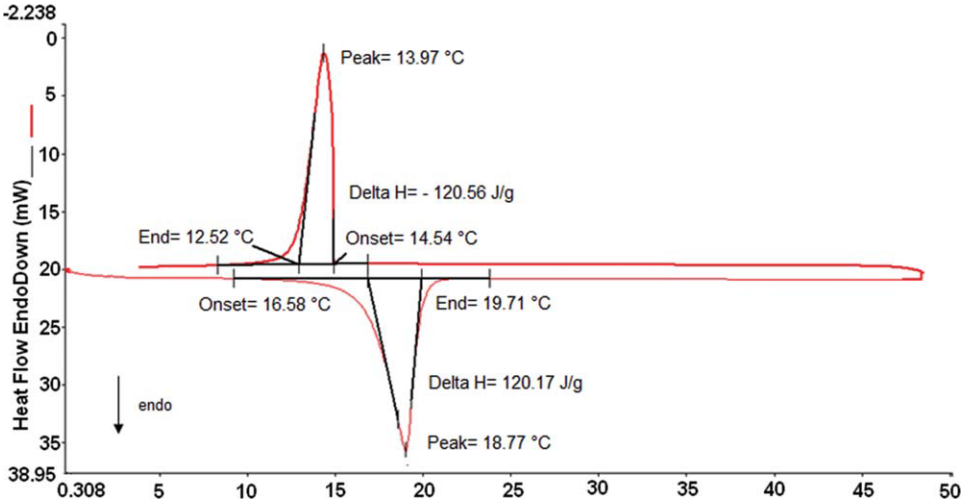

Figure 2 DSC curve of microPBA2 microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figures 1–3, respectively. It can be seen from Figure 1 that the phase change temperatures of the microPBA1 microcapsule are very close to that of hexadecane. MicroPBA1 melts at 17.36°C and crystallizes at 14.94°C, as the latent heats of melting and freezing of microPBA1 are measured as 83.60 and −86.79 J/g, respectively. The encapsulation ratio of hexadecane is calculated as 35.26% from eq. (1).

Figure 2 displays the DSC curve of microPBA2 microcapsules produced using ethylene glycol dimethacrylate as cross-linker. The phase change temperatures of the microPBA2 are 16.58°C for melting and 14.54°C for crystallization, as the latent heats of melting and freezing are 120.17 and −120.56 J/g, respectively. The encapsulation ratio of *n*-hexadecane was found as 50.69% for microPBA2. MicroPBA2 microcapsules are found to have more latent heat capacity than microPBA1 microcapsules.

Figure 3 represents the DSC curve of microPBA3 microcapsules produced using glycidyl methacrylate as cross-linker. MicroPBA3 microcapsules store 65.68 J/g and release −55.18 J/g energy during phase change processes. These microcapsules melt at 17.31°C and crystallize at 14.72°C. The encapsulation ratio was calculated as 27.70% according to eq. (1).

According to the latent heat of PCM formulation and the measured latent heat of microPCMs, the content of PCM formulation was 35.26%, 50.69%, and 27.70% for microPBA1, microPBA2, and microPBA3, respectively. These results are satisfactory for microencapsulated species.

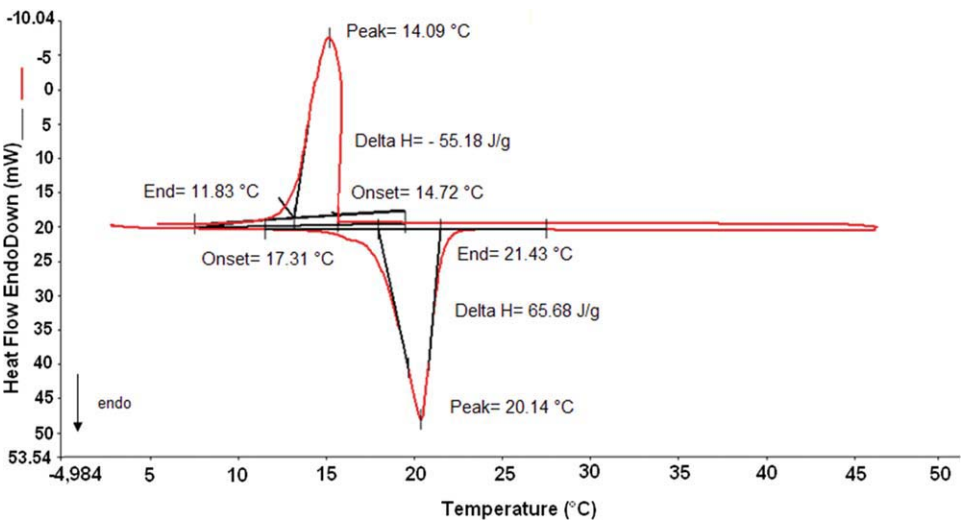

Figure 3 DSC curve of microPBA3 microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

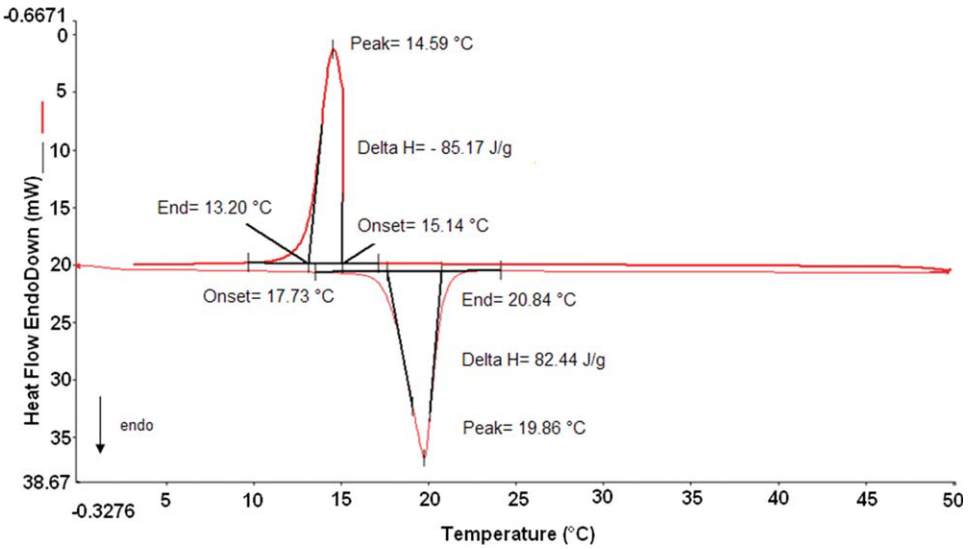

Figure 4 DSC curve of microPBA1 microcapsules washed at 40°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Microcapsules for textile materials should be stable on washing. For the efficacy of the produced microcapsules in textile materials, microPBA1 microcapsules were washed before applied to the fabrics at common laundering conditions for garments at 40°C. Figure 4 displays the DSC curve of washed microcapsules. The heat storage capacity and phase change temperatures of microcapsules were consistent at the end of washing. The result confirmed that the microcapsules were durable enough to secure stability against mechanical and thermal effects during washing in hot water.

Considerable amount of energy storage capacity, which is between 65 and 150 J/g, was obtained for microPBA microcapsules. MicroPBA3 microcapsules produced using glycidyl methacrylate cross-linker has the lowest heat capacity, whereas microPBA2 microcapsules produced using ethylene glycol dimethacrylate cross-linker has the highest value. Compared with literature, it was found that the produced microcapsules have extensive potential to be used in textile applications.[8,9]

The morphology and particle size distribution (PSD) of microcapsules

Figure 5 shows the SEM image of microPBA1 microcapsules produced using allyl methacrylate as cross-linker and the particle size distribution (PSD) of these microcapsules. It was seen that microparticles do not have regular spherical shapes. There is a single phase appearance, which can be commented as purity. The particle size distribution of microPBA1 microcapsules produced by using allyl methacrylate

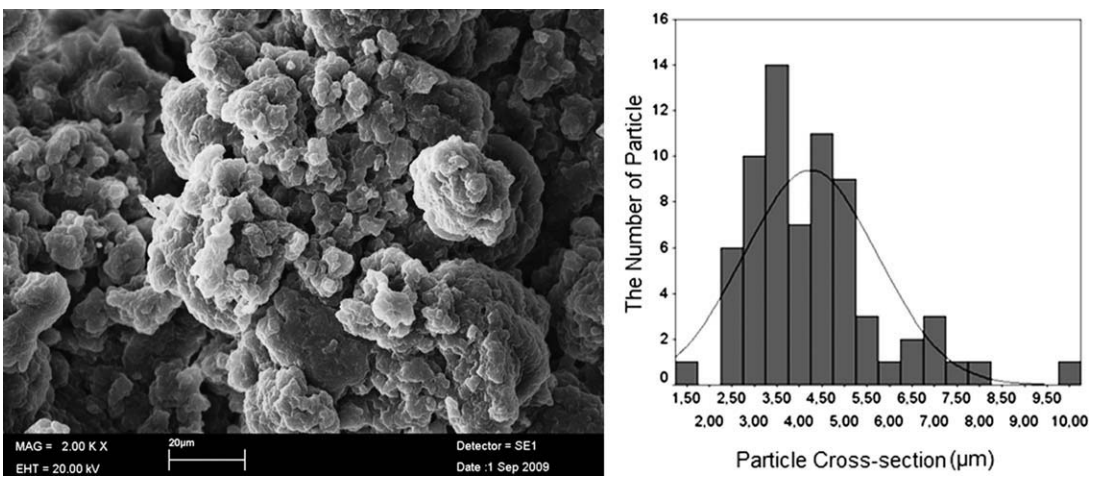

Figure 5 SEM images of microPBA1 microcapsules and its PSD.

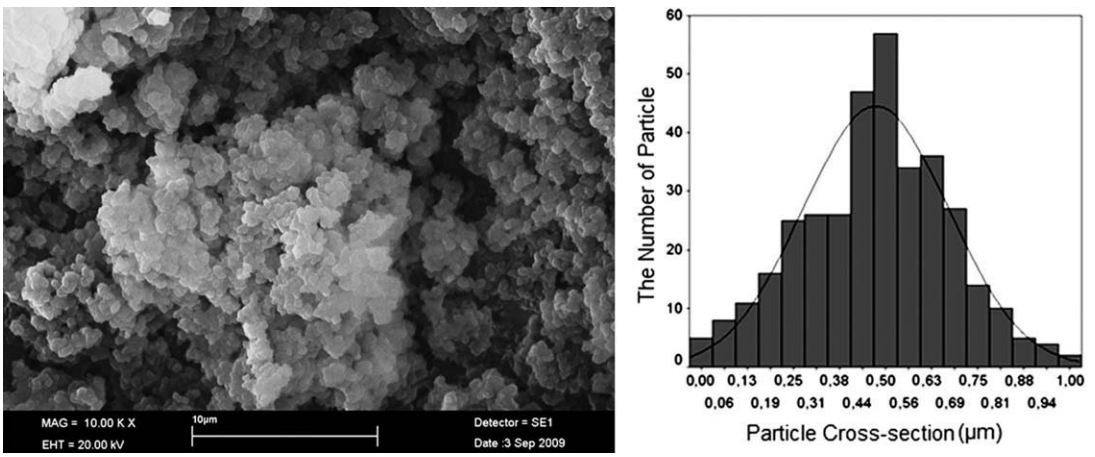

Figure 6 SEM image of microPBA2 microcapsules and its PSD.

as cross-linker is evaluated for the mean particle size. Although detection of particle distribution is difficult because of lack of fully regular particle formation, the size of the possible granular structures is measured using computer and PSD is plotted. It can be seen that the particle size distribution is broad and particle sizes varied from 1.5 to 10 μm, as the mean particle size was 4.25 μm.

SEM image of microPBA2 microcapsules are represented in Figure 6. MicroPBA2 microcapsules display granular particle formation. When these results are taken into consideration together with DSC results, it is determined that enthalpy values also increase with increasing granular structure. Granular structure as well as high-enthalpy results proved a high percentage of encapsulation. Besides, Figure 6 represents the PSD of microPBA2 microcapsules produced by using ethylene glycol dimethacrylate as the cross-linker. The mean particle size of microPBA2 microcapsules was 0.47 μm. The analysis of the size distribution shows that the particle size of microcapsules varies between 0.05 and 1 μm, exhibiting a uniform distribution. Microcapsules were characterized as nanocapsules related with mean particle size lower than 1 μm.

SEM image of microPBA3 microcapsules produced by using glycidyl methacrylate as cross-linker is given in Figure 7. It can be seen that microPBA3 microcapsules also do not have exact spherical forms. In addition, Figure 7 shows the PSD of microPBA3 microcapsules. Most of the particles had a size of 0.25 μm. The particle sizes varied from 0.13 to 1.5 μm, and the mean particle size was 0.54 μm.

FT-IR analysis of microcapsules

Chemical characterization of microPBA1, microPBA2, and microPBA3 microcapsules was carried out by FT-IR spectroscopy. The presence of *n*-hexadecane and PBA in PBA/*n*-hexadecane microcapsules was revealed by FT-IR spectra of *n*-hexadecane, butyl acrylate, and microPBA. Figure 8 shows the spectra for *n*-hexadecane, butyl acrylate, and microPBA1 microcapsules.

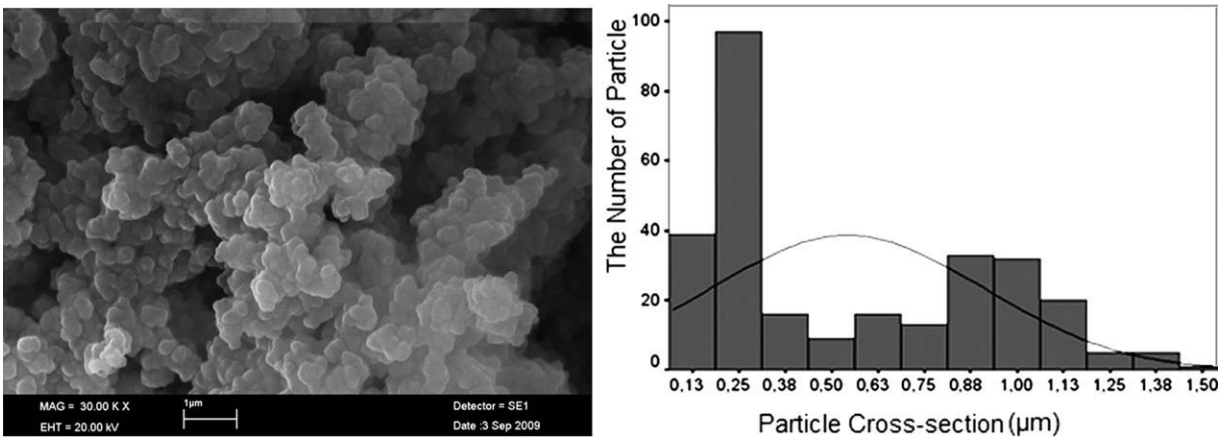

Figure 7 SEM image of microPBA3 microcapsules and its PSD.

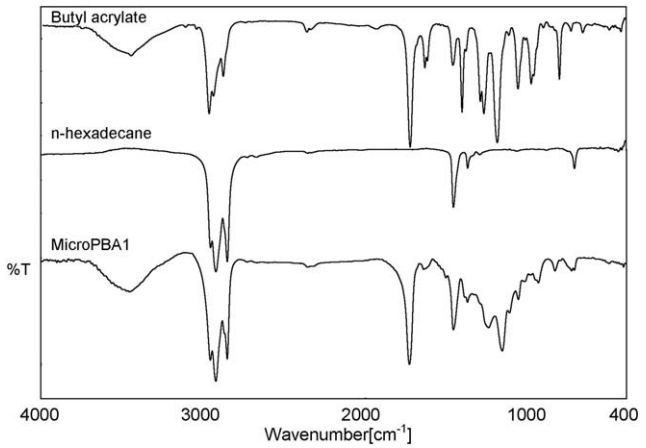

Figure 8 FT-IR spectra for *n*-hexadecane (a), PBA (b), and microPBA1 (c) microcapsules.

Information obtained from transmittance spectra of *n*-hexadecane, butyl acrylate, and microcapsules in Figure 8 are as follows:

- Peaks at 2956, 2916, and 1471 cm^{-1} in the pure *n*-hexadecane spectrum could be observed in the FT-IR spectra of microPBA microcapsules. This information proved the presence of *n*-hexadecane in the microcapsules with only very slight shifts.
- Peaks at 3434, 2958, 2919, and 1723 cm^{-1} in the pure butyl acrylate spectrum are also very slightly shifted in the microPBA microcapsules spectra, showing the presence of butyl acrylate groups in the microcapsules. However, C=C bond around 1626 cm^{-1} in butyl acrylate disappeared in the microcapsules, proving

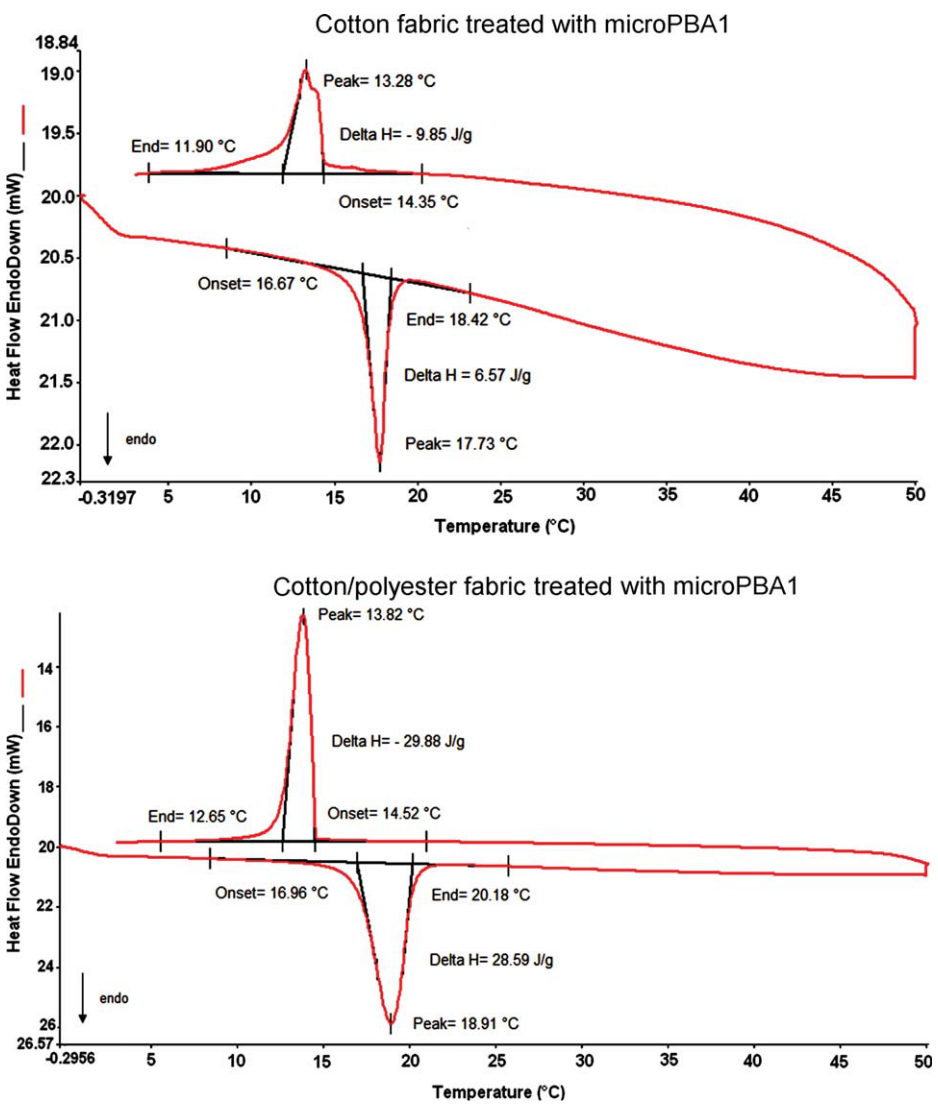

Figure 9 DSC curve of cotton fabric treated with microPBA1 microcapsules and cotton/polyester fabric treated with microPBA1 microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

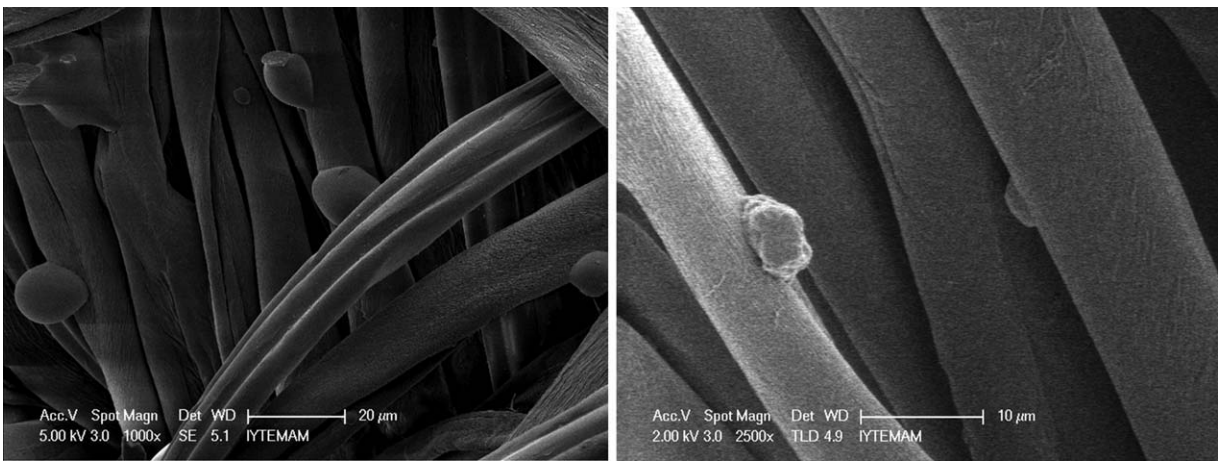

Figure 10 SEM micrographs for cotton fabric treated with microPBA1 microcapsules and cotton/polyester fabric treated with microPBA1 microcapsules.

polymerization. MicroPBA2 and microPBA3 microcapsules have been similarly characterized by FT-IR technique.

Thermal properties of the microcapsule-treated fabrics

Figure 9 shows the DSC curves of microcapsule-treated cotton and blend fabrics, respectively. It can be seen that the cotton fabric was capable of absorbing 6.57 J/g and releasing −9.85 J/g of heat if the microcapsules on the fabric undergo phase change processes. The cotton/polyester blend fabric is capable of absorbing 28.59 and −29.88 J/g of heat. The cotton/polyester fabrics have higher heat storage capacity than cotton fabric, although the same concentration of microcapsule is applied to the fabrics. It is concluded that the difference among the latent heat capacity of the fabrics impregnated with an aqueous solution of microcapsules are related to the amount of the microcapsules added on the fabric. The fabric construction and chemical compatibility of the fabric material with microcapsule shell material can influence the amount of the microcapsules added on the fabric. If the fabrics have enough porous construction that microcapsules can be placed into, heat storage capacity of the fabric increases. Cotton fabrics have little porous structure because of high fabric density. Thus, their heat capacities are lower than that of the blend fabric having more porous structure. Polyester is more compatible with acrylic microcapsules than cotton because of structural similarity. Because both polyesters and acrylic polymers have ester bonds at the backbone and at the pendant group, respectively. Moreover, OH groups present in the cellulosic cotton makes it more hydrophilic as the microcapsules are hydrophobic. Therefore, the fabrics made from polyester fiber can be more attractive material for microcapsules based on acrylic polymers. It is also obvious that the fabrics have considerable heat capacity for a low microcapsule concentration compared with the literature findings.[1,8,9,19,21] In addition, the microcapsules are found durable to secure stability against to 150°C curing temperature.

The melting and crystallization temperatures of microPBA1-treated fabrics are very close to that of microPBA1 microcapsules. The melting temperatures of the cotton and blend fabrics are 16.67°C and 16.96°C, respectively, whereas freezing temperatures are 14.34°C and 14.52°C, respectively.

Figure 10 shows the SEM micrographs for the cotton (on the left) and the blend fabrics (on the right). In both of the fibers, the microcapsules are incorporated on the backbone without causing any marked morphological change.

CONCLUSIONS

PBA microcapsules containing *n*-hexadecane are produced by using allyl methacrylate, ethylene glycol dimethacrylate, and glycidyl methacrylate as cross-linkers. The phase change temperatures of the microcapsules were very close to that of *n*-hexadecane. MicroPBA3 microcapsules produced using glycidyl methacrylate cross-linker has the lowest heat capacity, whereas microPBA2 microcapsules produced using ethylene glycol dimethacrylate cross-linker has the highest values. MicroPBA microcapsules have considerably high enthalpy to be enough for textile applications.

Encapsulated PCMs range from 0.47 to 4.5 μm in size. Microcapsules do not have exact spherical surface; they are most likely clusters. MicroPBA2 and microPBA3 microcapsules produced using ethylene glycol dimethacrylate and glycidyl methacrylate as cross-linkers are nanosize particles.

The microPBA1 microcapsules are incorporated to the fabrics by pad-cure method successfully. The microcapsule-treated cotton and blend fabrics are capable of absorbing 6.57 and 28.59 J/g of heat, respectively, if microcapsules on the fabric undergo a melting process. Cotton/polyester blend fabric has been found more suitable for microcapsules application than cotton fabric.

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