Iranian Polymer Journal
19 (4), 2010, 277-286

Available online at: http://journal.ippi.ac.ir

Preparation of Phase-change Material Microcapsules with Paraffin or Camel Fat Cores: Application to Fabrics

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Received 16 August 2009; accepted 1 March 2010

ABSTRACT

Samples of phase-change materials (PCM) microcapsules containing solid paraffin or camel fat as core materials were synthesized by in situ polymerization using melamine-formaldehyde as shell material. The microcapsules were made in two consecutive steps, emulsification of PCMs in water and then, encapsulation. Differential scanning calorimetry (DSC), Fourier transform infra-red (FTIR) spectroscopy, optical and scanning electron microscopy (SEM) and particle size analysis were used to characterize the microcapsules. A simple test method was devised to visually examine the oil seepage and leaking from microcapsules. For paraffin microcapsules the effect of agitation speed, through a limited range, was examined on the size of microcapsules during the formation of pre-polymer. The microcapsules were prepared from camel fat by the similar procedure used for the paraffin microcapsules. The microcapsules were spherical in shape with harsh surfaces as observed by SEM. The average diameter of camel fat microcapsules with 95% confidence limits is 1515±199 nm and that of paraffin is 1600±341 nm. The shell resin was strong and stable enough to prevent the liquid oils from seepage and leaching at 80°C. The effect of prepared camel fat microcapsules on the delay of heat was determined through examining a covered polyester/viscose-fibre fabric. The loaded fabric samples with 10% (w/w) camel fat microcapsules delayed the rise of temperature of the covered thermometer when exposed to heat at 50°C oven. Newton's law of cooling was applied to determine the delay in temperature change.

Key Words:

phase-change-materials;
microcapsule;
melamine-formaldehyde;
fabric;
camel fat;
paraffin.

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INTRODUCTION

This work faces two different technologies; namely; microencapsulation and phase-change materials application which are the undergoing research topics in the academia and industry. To follow, the introductory section is divided into two parts.

Microencapsulation by In Situ Polymerization

Microcapsules are tiny particles of solid, liquid or gas with diameters smaller than 1 mm and larger than 1μm, covered with shell materials that are relatively strong and thin [1]. Considerable numbers of core and shell materials are now used to produce commercial microcapsules for different applications. This field of science and technology is growing very fast. According to Thies [1], throughout the world research and development activities are

dedicated to advancing microencapsulation technology. Dyes, drugs, fragrances and phase-change materials are very common materials for core and gum Arabic, amino plastics and ethyl cellulose are well used as shell materials. For the sake of brevity, a few are mentioned here [2-5] to show the diversity of the works using formaldehyde as the main ingredient for shell material.

Hong et al. [6] used melamine and formalin to produce microcapsules containing fragrant oil, (Migrin oil) as core material, by in situ polymerization. The sizes of spherical microcapsules produced were less than 10 μm, with a relatively narrow size distribution. It was found that the fragrant in the microcapsules has had a longer shelf-life.

Lee et al. [7] successfully synthesized microcapsules containing fragrant oil (Foral oil) by in situ polymerization using melamine/formaldehyde (M/F) as shell material. The encapsulation efficiency and other physical properties were analyzed with varying formaldehyde/melamine (F/M) molar ratios and pH of the emulsion medium. The size of particles produced ranged between 12 and 15 μm. It was found that both pH and F/M molar ratio have influence on the surface morphology of the microcapsule and the encapsulation efficiency. The liquid-liquid phase separation of methylolmelamines and formation of M/F precursor particle explain the surface morphology and encapsulation efficiency.

For appropriate strength and stability in surrounding medium, melamine-formaldehyde resin is used by Yuan et al. [8] to synthesize microcapsules containing dicyclopentadiene, as healing agent, for self-healing composites. The mean diameters of the microcapsules fall in the range 65.2-202.0 μm, when the agitation rate is in the range of 250 to 500 rpm. It is believed that increasing the surfactant concentration can reduce the size of microcapsules.

Phase-change Materials

Phase-change materials (PCM) are used for storing or releasing energy because of their high heat of fusion (latent heat). Now organic and inorganic PCMs are available for different types of applications [9]. Among different methods of storing energy, using PCMs for several applications, encapsulation is often used. In a number of research works [10-12] melamine/formaldehyde (M/F) was used as shell material and among different PCMs for thermo-regulating textile materials, alkanes with melting temperature in the range of 10°C to 50°C were used [12]. The description of the materials with proper properties are found in the literature, which has to be environmentally safe with high heat of fusion and melting temperature close to ordinary room temperature. In order to show the scope of the previous works, using formaldehyde as the main ingredient for the shell materials, recently published papers are indicated below.

Choi et al. [10] prepared microcapsule from tetradecane as core material, and melamine/formaldehyde (M/F) resin was used to form the shell. It was shown that the capsules had a high latent heat of fusion, uniform shape and size, excellent durability and good performance for the potential application in heat transfer.

Crystallization and prevention of supercooling of *n*-alkanes were studied by Zhang et al. [11]. In this study microcapsules were synthesized containing *n*-octadecane, *n*-nonadecane and *n*-eicosane as core materials and urea or melamine formaldehyde polymer as shell materials. The crystal system of the microencapsulated *n*-alkane was the same as that of the bulk and the melting temperature did not change. The cooling behaviour of microencapsulated *n*-octadecane, in DSC, depended on the average diameter of microcapsules. The measured maximum degree of supercooling was approximately 26°C at heating and cooling rates of 10°C/min.

Shin et al. [12] developed thermoregulating fabrics using microencapsulated PCM. Melamine/formaldehyde (M/F) microcapsules containing eicosane were prepared by in situ polymerization. The microcapsules were spherical in shape with average diameter less than 10 μm and were stable under stirring in hot alkaline water. The microcapsules were added to polyester knit fabrics by a conventional pad-dry-cure process using a proper binder.

In our previous work [13] we found that camel fat can be used as a natural PCM. In that work a specific amount of PCMs, including paraffin and camel fat,

were spread over fabrics and examined. By spreading waxy PCM over the fabric freely, there are always the problems of seepage and leaching. The purpose of the present study was to examine the possibility of producing camel fat microcapsules and determining their effects when they are coated over fabrics with the help of a printing binder which has not been reported before.

We used paraffin for its easy availability and low cost, and it guided us to select the proper procedure for camel fat microencapsulation. For protection through high temperature exposure of equipments and industrial applications, paraffin with higher melting point may also be used.

EXPERIMENTAL

Materials and Methods

Acetic acid and sodium hydroxide as pH controller, sodium dodecyl sulphate (SDS) as an emulsifier, polyvinyl alcohol as a viscosity improver and paraffin as core materials were used as received. All these chemicals were from Merck, Germany. Formalin (41.5% formaldehyde) was commercial grade and melamine was purchased from Bojnurd Petrochemical Industry, Bojnurd, Iran. Camel fat was supplied by a local producer of animal protein productions. Plain woven fabrics used were polyester/viscose (65% polyester 35% viscose, 170 g/m^2) shirting, supplied by a domestic fabric producer. Binder, Alcoprint ptu® was supplied by Ciba (Switzerland).

Preparation of Paraffin Emulsion

Microcapsules were prepared in two consecutive steps. The first step was the preparation of oil-in-water emulsion. In this step 25 g solid paraffin was added gradually to 160 mL water in a beaker containing 2.9 g/L sodium dodecyl sulphate (SDS), while homogenizer was running at 2500 rpm at 80°C. During this period a small amount of polyvinyl alcohol (1.8 g/L) was added to stabilize the emulsion. The homogenizer speed then increased to 6000 rpm and maintained at this speed for 30 min. An emulsion that was found to be generally stable at least for 12 h was employed immediately for the second step. The homogenizer used was Polytron PT3100, from Kinematica, Switzerland.

Preparation of Camel Fat Emulsion

Exactly similar to the method for paraffin emulsion preparation, emulsion of camel fat in water (25 g camel fat in 160 mL water) was prepared using SDS as emulsifier, by a homogenizer, with final speed of 6000 rpm at 80°C. A small amount of polyvinyl alcohol (1.8 g/L) was added to increase the solution viscosity and to stabilize the emulsion.

Encapsulation

The second step of microcapsule preparation was prepolymer preparation and encapsulation. The described method by Shin et al. [12] was followed. A solution of 0.66 mol/L melamine in water was prepared and 14.5% formalin of 41.5% was added. The pH was controlled at the range 8.5-9 with aqueous solution of 10% sodium hydroxide. The temperature of the solution was adjusted to 70-75°C, and it was mixed for 1 h using a mechanical mixer at 250 rpm or the speeds that will be indicated in the later sections. Then, the paraffin or camel fat emulsion in water was added to the above solution and, by adding diluted acetic acid the pH of the solution lowered to 5-5.5. The agitation continued for 1 h, and then the temperature was reduced. The resultant microcapsules were collected on a filter paper, washed several times with distilled water, filtered and dried in an oven at 35°C. The agitator was Polymix with anchor type blade, from Kinematica, Switzerland.

Application of Microcapsules to Fabrics

Solutions of Alcoprint ptu® (5 g/L) in water was prepared by gradually mixing and stirring at room temperature, then the two mixtures with different concentrations of camel fat microcapsules in the binder solution were prepared. The pastes were then spread over the fabrics by a blade. After curing, the microcapsule add-on was 0.6 and 10 w/w% of fabrics. For the paste being cured, the loaded fabrics were placed in an oven of 150°C for 15 s.

Characterizations

The particle size and size distribution of the

microcapsules were determined using particle analyzer (SEMATech, SEM 633, France). Distilled water was used as the medium and the temperature was 26°C with 100 μ pinhole, 90° angle and 632.8 nm wavelength. Microcapsules were also examined by an optical microscope (Zeiss, Germany) and a scanning electron microscope (SEM) (TESCAN, Brno, Czech Rep). A diffrential scanning calorimeter (DSC, Polymer Laboratories, England) was used for measuring thermal behaviour of the PCM samples. Fourier transform infrared (FTIR) spectra of the samples were obtained using a Bruker Equinox 55 Instrument, USA. A Lutron HT-3009 (Taiwan) temperature measuring device was used for measuring the thermal behaviour of the systems.

Visual Testing of Microcapsules

In order to test visually the absence of paraffin or fat on the surfaces and to check the presence of the core materials after the breakage of microcapsules, a testing procedure was developed as following: about 0.2 g of microcapsules was weighed and placed over an oil absorbing paper and then it was transferred over a hot plate. The plate temperature was adjusted at 80°C.

The microcapsules were agitated for about 5 min and the paper was watched for the change of its colour (Figures 1a and 1c). Then the microcapsules were pressed to break by the end of a spatula. Due to the breakage of the microcapsules the melted paraffin or camel fat were extracted out which was followed

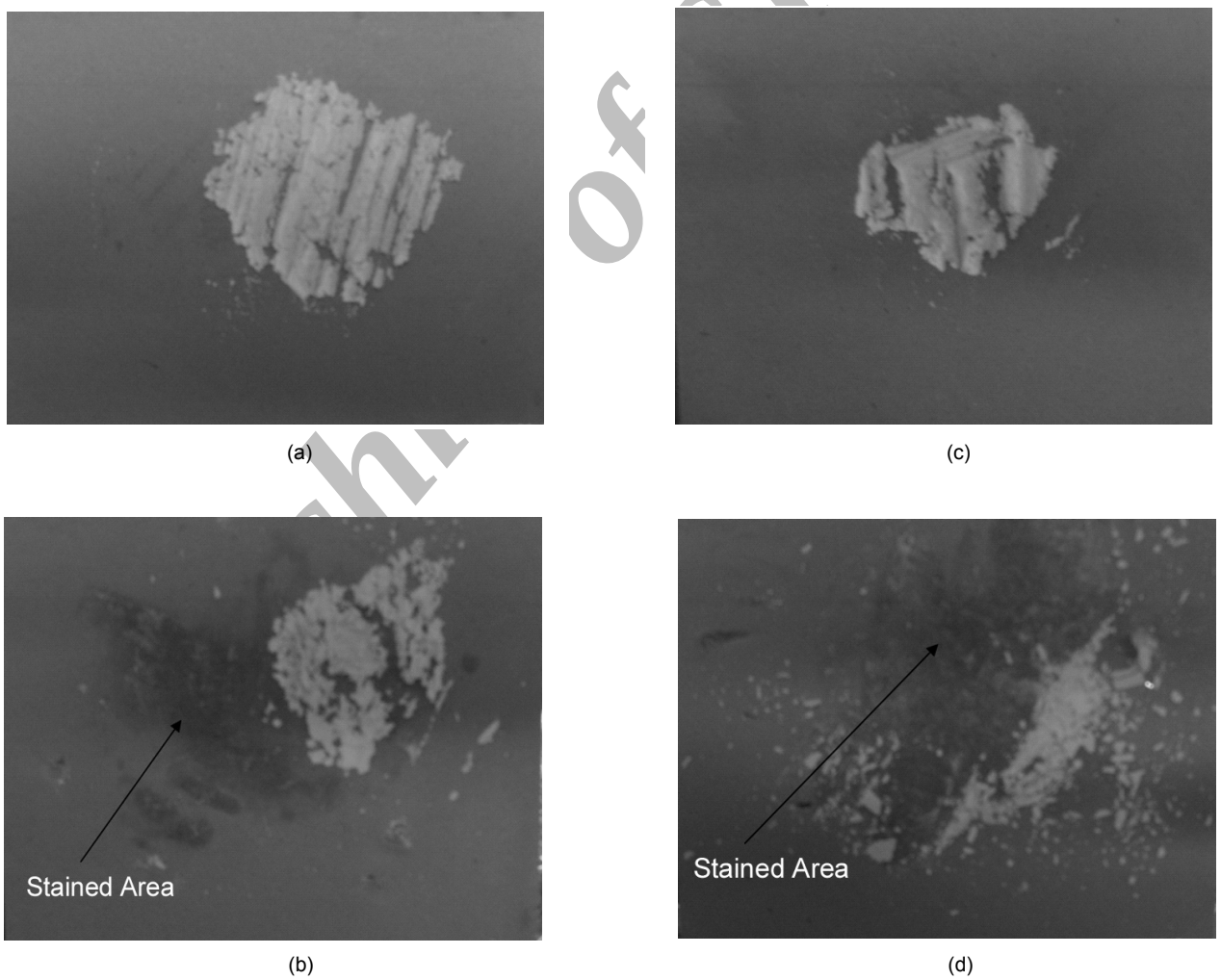

Figure 1. Photographs of microcapsules of (a) camel fat before applying pressure, (b) camel fat after pressing, (c) paraffin before applying pressure, and (d) paraffin after pressing with a spatula on oil absorbing papers over a hot plate at 80°C.

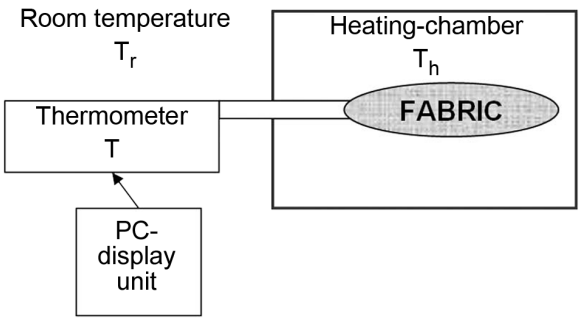

Figure 2. Experimental arrangement for determining the delay in temperature rise of the thermometer probe.

by changes in the paper colour and its gloss (Figures 1b and 1d). The oil mainly changes the paper glossiness that may not be well distinct in the photographs shown. By reweighing the paper and the broken microcapsules separately, the amount of oil in the microcapsule could also be determined.

Testing Fabrics Behaviour During Heating Cycle

Samples of fabrics were wrapped around the probe of the temperature measuring device. The temperature of the probe was stabilized at room temperature and then the probe with the fabric was placed in an oven that was stabilized at 50°C. The temperatures were measured and automatically recorded at intervals of 2 s after placing the probe in the oven. To normalize the results of the temperature measurements, the measured temperatures were then divided to room temperature (T_r) and the relative changes of temperature (T/T_r) as reported

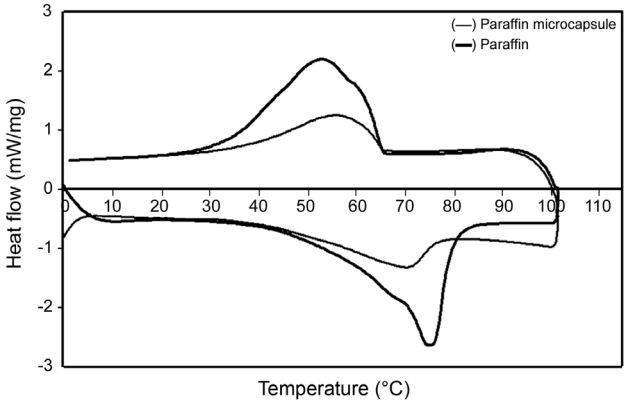

Figure 3. DSC thermograms of paraffin and its microcapsules.

here. The probe without any covering fabric was also examined. Figure 2 shows the experimental arrangements.

RESULTS AND DISCUSSION

Figure 3 shows representative DSC thermograms of paraffin and microcapsules containing paraffin during heating and cooling cycles. Parameters extracted from the thermograms are summarized in Table 1. The melting temperature of paraffin in bulk is 74.9°C and in microcapsule form is 70.1°C. This finding was re-examined and the difference in the melting temperature (4.8°C) was confirmed. This reduction of melting point, probably, can be the result of unavoidable contamination of paraffin with

Table 1. Thermal properties of paraffin, camel fat and their microcapsules from DSC data.

Materials	T_m (°C)	H_m (J/g)	T_c (°C)	H_c (J/g)
Paraffin	74.9	-204.6	53.0	199.7
Paraffin microcapsule	70.1	-63.2	55.8	72.7
Camel fat	14.8	-13.1	7.0	12.1
	53.1	-56.1	31.5	31.5
Camel fat microcapsule	10.0	-	7.1	3.6
	31.2	-0.8	29.3	11.9
	51.3	-28.4	-	-

T_m : peak temperature on DSC heating curve; H_m : enthalpy on DSC heating curve; T_c : peak temperature on DSC cooling curve; H_c : enthalpy on DSC cooling curve.

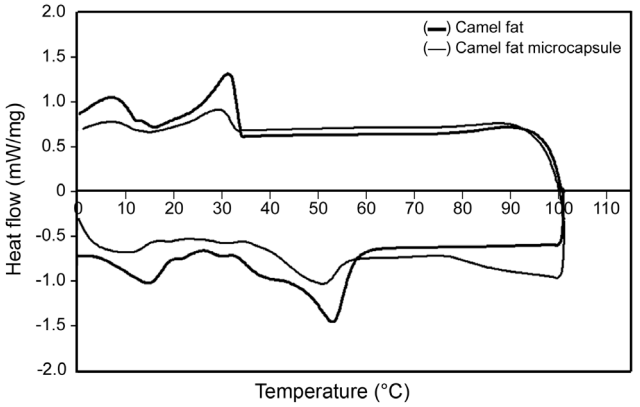

Figure 4. DSC thermograms of camel fat and its microcapsules.

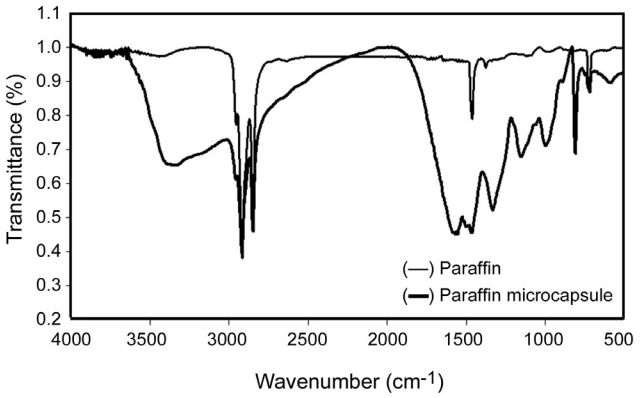

Figure 5. FTIR spectrum of paraffin and its microcapsules.

chemicals, such as dispersing agents, during emulsification and microcapsule synthesis. Zhang et al. [8] carried out three heating-cooling cycles for each sample and reported that the melting temperature of the *n*-alkanes in the microcapsules was the same as in the bulk.

Considering that the M/F resin does not have any phase-changes in the temperature range of -20 to 100°C, the content of the microcapsules can be estimated from the melting (heating cycle) or crystallization (cooling cycle) enthalpies. Due to melting enthalpy dependence on the thermal history of the samples, the contents calculated from first melting cycle and crystallization cycles are not equal. The content of paraffin in microcapsules calculated from enthalpies during cooling is 36% and from enthalpies during heating cycle is 31%.

Figure 4 shows the DSC thermograms of camel fat and its contained microcapsules. The thermal parameters deduced from thermograms are summarized in Table 1. Camel fat has multiple melting and crystallization temperatures in bulk and in microcapsules. Similar to paraffin, the melting temperature of camel fat in microcapsules is lower than in bulk form. From the enthalpies, the content of camel fat in microcapsules is calculated to be 42% from heating cycle enthalpy and 35% from cooling cycle enthalpy.

FTIR spectra of paraffin wax and paraffin microcapsules are shown in Figure 5. The carbon-hydrogen stretching and bending absorption bands are at 2940-2855 cm^{-1} and 1470 cm^{-1}, respectively. The symmetric carbon-hydrogen bending absorption of the CH_3 group at 1380 cm^{-1} and the CH_2 rocking absorption band at 725 cm^{-1} confirm the linear saturated aliphatic structure of the paraffin wax [14]. In Figure 5 for the microcapsules, in addition to the paraffin bands, there are peaks at 3300 cm^{-1} to 3500 cm^{-1} due to N-H stretching vibration band and at 1650-1580 cm^{-1} due to the N-H bending band [9]. These peaks confirm the presence of melamine/formaldehyde resin and paraffin in the microcapsules.

FTIR spectra of camel fat and its microcapsules are shown in Figure 6. For the camel fat, there are peaks at 1740 cm^{-1} and 1250-1000 cm^{-1} which are due to the stretching vibration bands of carbonyl in un-conjugated ester and the carbon-oxygen single bond, respectively. The spectrum also shows the characteristic peaks of aliphatic straight chain. According to Figure 6, in FTIR spectrum of microcapsules in addition to camel fat characteristic

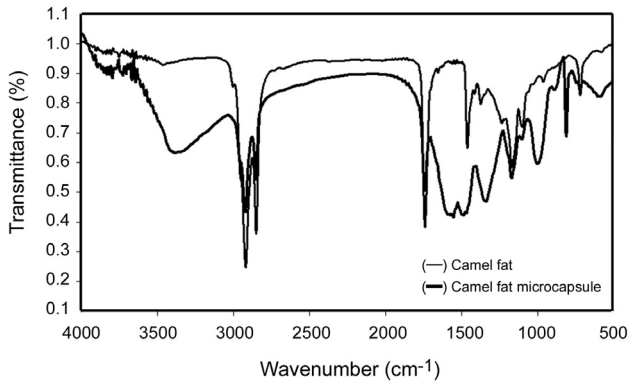

Figure 6. FTIR spectrum of camel fat and its microcapsules.

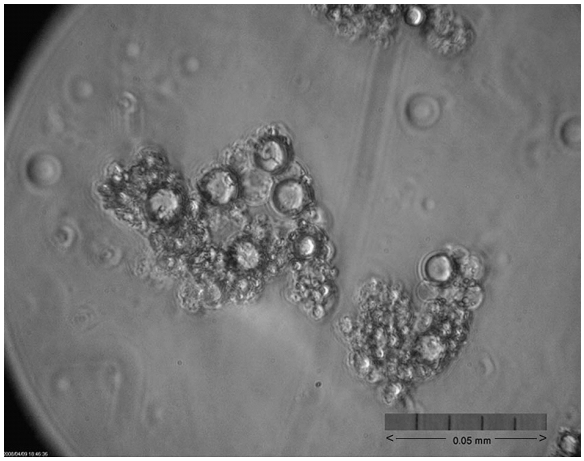

Figure 7. A typical optical micrograph of paraffin microcapsules.

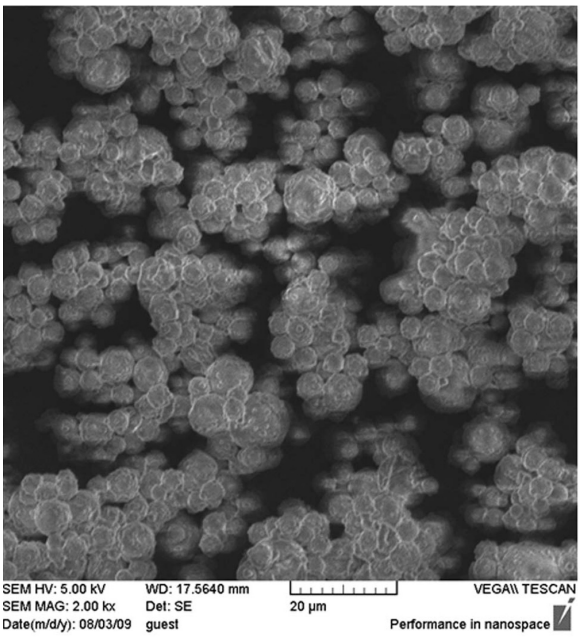

Figure 8. A typical SEM micrograph of paraffin microcapsules.

bands, N-H characteristic bands are also observed. These peaks confirm the presence of melamine/ formaldehyde resin and camel fat in the microcapsules.

The microcapsules were also tested visually according to the procedures explained earlier, when the microcapsules were heated to 80°C and observed before and after the breakage. There was no mark or spot of paraffin or camel fat (oily stain) observed on the surface of the papers. Figures 1a and 1c show the plain papers before the breakage of microcapsules, and extraction of paraffin and camel fat and the oil-stained papers after pressing and breaking the microcapsules are shown in Figures 1 b and 1d.

Figure 7 shows a typical optical micrograph of paraffin microcapsules. The spherical microcapsules look flat and tiny which are observed with a light microscope. The size of the microcapsules is in the range of a few micrometers. Using SEM with higher resolution power and greater field depth, the spherical microcapsules are shown in Figure 8.

There are several important factors that might have affected the size of microcapsules including the concentration of emulsifier and the rotational speed of agitation, both during emulsification of the wax and prepolymer formation [15]. Increase in the concentration of emulsifier tends to decrease the size of droplets through the reduction of the surface tension, leading to increased specific surface areas. Increasing the rotational speed of the stirrer improves the shear stress to act on the dispersed phase and reduces the size of the droplets. The size of micro-capsules, in addition to the size of the paraffin or camel fat particles depends on the stability of the particles and the thickness of the shell, which the latter depends on the amount of prepolymer precipitated on the surface of the particles.

The multitude of factors that have affected the size of the microcapsules persuaded us to do a few preliminary tests. It was soon found in this work that the number and the levels of these parameters have exceeded beyond considerations. Then, only the effect of agitation speed on the size of microcapsules during the formation of pre-polymer was estimated. The results of these preliminary tests are presumably useful for the future design in determining the effects of various parameters which are ignored here and need underlying vast theoretical backgrounds.

Figure 9 shows the distributions of the diameter of paraffin microcapsules prepared at different agitation speeds. The diameters are not changed considerably at different speeds, in the present range. At 150 rpm the average diameter is 1583 nm, at 250 rpm the average diameter is 1600 nm and at 650 rpm the average diameter is 1932 nm. Considering the variation of the sizes in each group, the differences in

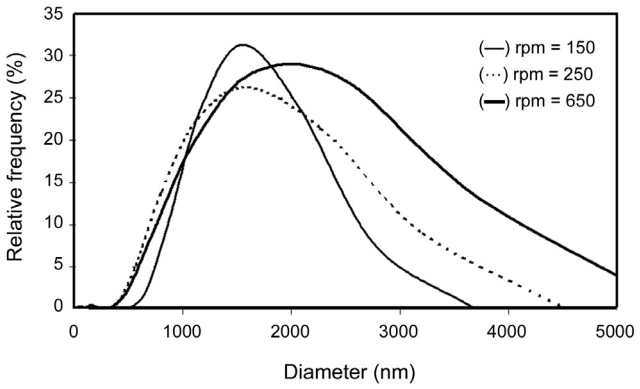

Figure 9. Distributions of the diameter of paraffin microcapsules prepared at different agitation speeds.

diameters are not statistically significant at 95% confidence limits. This experiment indicates that for reducing the size of microcapsules the agitation speed must be increased more than the range tested in this preliminary experiment.

Figures 10 and 11 show SEM micrographs of paraffin and camel fat microcapsules, respectively in which spherical particles with harsh surfaces are observed. In a separate test a sample of microcapsules were washed for 45 min in an aqueous solution of 0.5% SDS and examined by SEM. The harshness of the surfaces did not change. Probably small

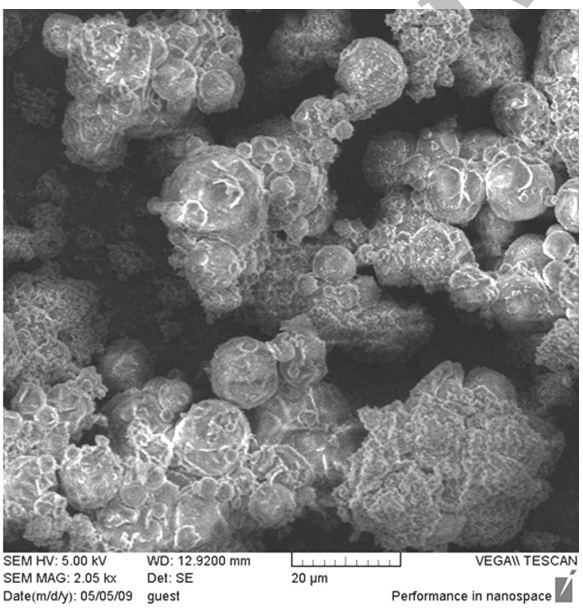

Figure 10. SEM photomicrograph of paraffin microcapsules.

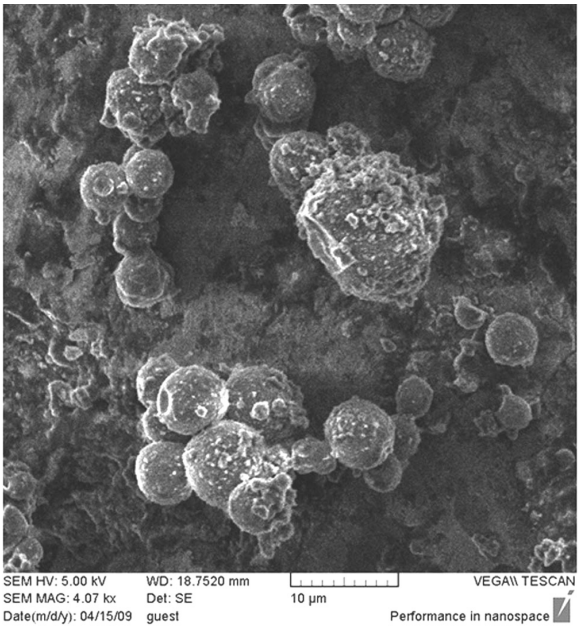

Figure 11. SEM micrograph of camel fat microcapsules.

microcapsules aggregated and formed the larger spherical microcapsules.

Figure 12 compares the distributions of the diameters of paraffin and camel fat microcapsules, as determined by particle size analyzer. The average diameter of camel fat microcapsules at 95% confidence limits is 1515±199 nm and that of paraffin is 1600±341 nm which is not considerably significant. Having successfully prepared camel fat microcapsules, its effect on the delay of heat through a covered fabric was examined in a subsequent experiment.

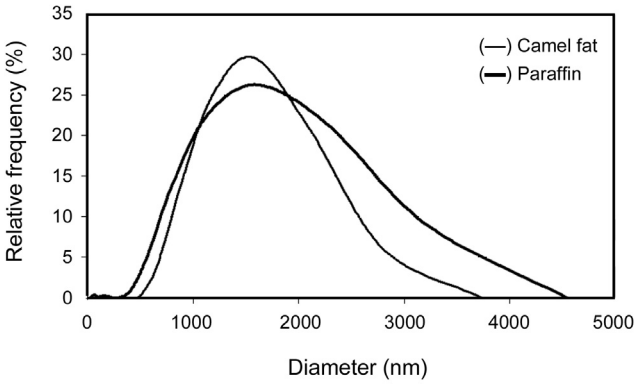

Figure 12. Comparison between the distributions of the diameters of paraffin and camel fat microcapsules.

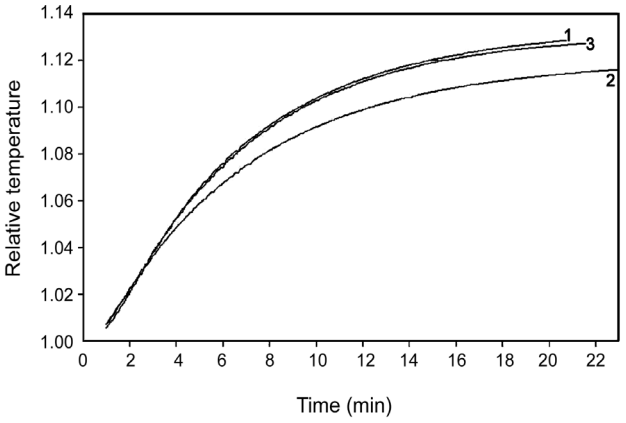

Figure 13. Temperature changes of covered thermometer by fabrics: (1) without PCM, (2) with 10% PCM, and (3) with 0.6% PCM in heating oven.

Figure 13 shows the behaviour of the fabric-systems during a heating cycle. When the amount of camel fat microcapsules is low (0.6%) its effect on the delayed temperature rise is not significant. When the amount of camel fat microcapsules increases to 10%, then its effect on the delayed changes in the temperature of the probe is significant. It seems that in the earlier periods, the effect of PCMs is more pronounced. In heating cycle after about 18 min the temperature of the uncovered probe increases by more than 10% while for those covered with PCMs the changes are considerably below 10%.

We tried to apply the Newton's law of cooling [16], similar to the previous work [13], to determine the extent of temperature change, when the thermometer probe is exposed to heat. It was found that the temperature of the probe (T) can be shown by following equation:

$$T = T_h - (T_h - T_r)\exp(-st)$$

where T_r is the room temperature and T_h is the oven temperature, t is the time and s is related to the several assembled properties such as density of the covering, heat transfer coefficient and specific heat of covering, etc. The temperatures of different compartments are designated in Figure 2. The value of s is considered as a parameter to indicate the delayed rise in temperature. Using the unit of Kelvin for temperatures and minutes for the time, the value of s was calculated using Curve Fit® computer software. The value of s is 0.16 for the fabric loaded with 10% PCM microcapsules and 0.14 for plain fabric and the fabric loaded with 0.6% PCM. In all cases the correlation coefficients are more than 0.98.

CONCLUSION

In the present study melamine/formaldehyde resin is used as shell material to prepare microcapsules containing paraffin and camel fat. It is found that microcapsules containing camel fat or paraffin wax can be made easily. Fabrics loaded with a considerable amount of camel fat microcapsules (10 w/w%) would delay the temperature rise of a probe exposed to 50°C environment by less than 10%. These fabrics may be used where short time protection is required against sudden increases of temperature, which is a point of interest in the production of smart fabrics.

ACKNOWLEDGEMENT

The authors would like to express their gratitude to INSF (Iran National Science Foundation, Proj. No. 8411612) for the financial support. We would like also to extend our appreciation to Mr F Mazaheri for his help and guidance in emulsion preparation. The laboratory works for preparation of paraffin microcapsules were performed by Mrs E Misaghi whom we would like to express our gratitude.

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