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New Approach of Phase Change Material Encapsulation through *in situ* Polymerization to Improve Thermo-Regulating Property of Cellulose

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To incorporate thermal comfort in fabric by the use of latent heat storage, micro-encapsulated phase change material is the most efficient way of storing thermal energy. This paper reports a study on the new approach of encapsulation by using three concentrations of 2.5, 5 and 7.5 wt % of polyethylene glycol-1000 used as a phase change material through *in situ* polymerization. PEG-1000 microcapsules were characterized by the optical microscope, scanning electron microscope, Fourier transform infrared spectroscopy analysis and differential scanning calorimeter studies. By measuring differential scanning calorimeter results, the highest thermal energy storage attributed for 5 % PEG coated fabric than binder coated fabric that is 3.96 kJ g^{-1} and it plays a vital role to enhance the thermo-regulating property of cotton fabric. Samples were tested for thermo-regulating properties *i.e.* air permeability, thermal resistance, thermal energy storage, tensile and tearing strength testing by independent measurement way. Phase change material treated fabric shows good thermo regulating property, when applied on textile materials.

Keywords: Phase change material, Thermal resistance, Thermal energy storage, Micro-encapsulation, *in situ* Polymerization.

INTRODUCTION

Fundamental principles of functional textiles have been developed to enhance textile performance and to protect textile industry from extreme environmental conditions. The demands of dynamic thermo-regulating fabric have attracted more and more attention [1]. Thermo-regulated textile is a smart textile material that can change its temperature according to the environment. Phase change material has been used to produce thermo-regulated textiles to improve thermal properties of textile garments. Phase change materials can absorb, store and release large amounts of latent heat over a defined temperature range while undergoing phase changes and their application in thermal energy storage has been well known in many fields and it is one of the most important techniques to make the renewable energy and increase percentage of the energy efficiency [2,3]. It is reported that incorporation of phase change materials in textiles will perform buffering effect keeping the skin temperature constant against extreme weather hence prolonging thermal comfort for the wearer and is also claimed that using phase change materials can decrease the fabric thickness required to protect the human body from cold environment [4,5]. When phase change materials are applied in textile, phase change materials have to be put into micro-capsules. Otherwise they will eventually drip off clothing when they melt [6]. Microencapsulation is the process of enveloping microscopic sized droplets or particles in a shell material for the purposes of protection or controlled release, because phase change material-containing microcapsules must be durable and safe through the finishing process. The phase change material encapsulated materials are embedded with conductive medium and these medium can be designed in a variety way to provide enhanced thermal management [7]. A literature survey on micro-encapsulated phase change materials indicates that the most suitable methods include *in situ*, interfacial and suspension polymerization methods for chemical processes and simple or complex phase coacervation for physico-chemical processes and spray-drying for the mechanical processes [8,9]. Among these, *in situ* polymerization is the most widely used for the encapsulation of phase change materials capable of producing strong capsules and also suitable for textile applications [10,11]. *in situ* Polymerization is similar to interfacial polymerization, except there are no reactive monomers in the organic phase and all polymerization

takes place in the continuous phase rather than in the interface of the droplets as in interfacial polymerization [12]. At present organic and inorganic phase change materials are used for different type of applications [13]. Polyethylene glycol is one of the most essential polymeric stable-liquid phase change material. Thus, PEG with a molecular weight comprised between 600 and 1500 g mol^{-1} have melting points in the temperature range between 17 to 35 °C and a melting enthalpy between 120 to140 J g^{-1} [14]. In addition, it has a good biocompatibility because of its intrinsic molecular structure and therefore it is frequently employed in biomaterials [15]. Thermal energy storage can be defined as the protecting of thermal energy in temporary way inside the shape of warm or cold substances for later usage. It bridges the time gap among energy necessities and energy supply [16]. Among the various heat storage techniques of interest, latent heat storage is particularly attractive due to its ability to provide a high storage density at nearly isothermal conditions. Phase-change thermal energy storage systems offer other advantages, such as a small temperature difference between storage and retrieval cycles, small unit sizes and low weight per unit storage capacity [17,18].

The focus of this research was to develop and improve the thermo regulating property of cotton fabric by using phase change material urea-formaldehyde microcapsules prepared through *in situ* polymerization. For conducting this research, three concentrations of 2.5, 5 and 7.5 wt % of PEG-1000 was used and the highest thermal energy attributed for 5 % PEG-1000. The treated fabrics were characterized with respect to their morphology, while thermal, air-permeability, tensile and tearing strength properties were evaluated for practical application.

EXPERIMENTAL

In this study, 100 % bleached, scoured cotton fabric (poplin) plain weave (140 ends and 64 picks cm^{-1}; count is 20 × 20, with a weight of 240 g m^{-2}) was used and it was not subjected to any type of finishing treatments. Then it was further washed with a solution containing 2 g L^{-1} sodium carbonate and 2 g L^{-1} non-ionic detergent at 20 min and followed by one cycle of cold water rinsing. Polyethylene glycol-1000 (Fig. 1) and properties are shown in Table-1. Sodium salt of dodecyl benzene sulfonic acid, polyvinyl alcohol, urea, formaldehyde was purchased from Sigma Aldrich, Inc. and Span® 80, ammonium chloride, acetone, 1,3-benzenediol, sodium carbonate, Ammonia liquor and acrylic based binder was purchased from BASF. These chemicals were used without further purification after receipt from supplier.

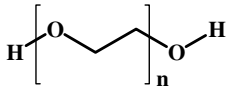

Fig. 1. Polyethylene glycol

Preparation of microcapsules: For preparation of micro-encapsulated system, a unique encapsulation procedure was followed by modifying the methods used [19]. Microcapsules were prepared by *in situ* polymerization of urea-formaldehyde resins encapsulating the core material (PEG-1000) mentioned above. To start, at first microencapsulation was made for 2.5 wt % of PEG-1000. At room temperature (20-24 °C), 2.5 g PEG-1000 and 2 g of sodium carbonate were mixed in a 100 mL distilled water and mixture was stirred for 15 min at 500 rpm by magnetic stirrer and the temperature was raised to 40 °C through hot plate, while two separate layers of water and PEG was observed in the beaker. A three-neck reactor is placed in ice cold water bath to avoid early polymerization reaction by maintained temperature. An aqueous pre-polymer solution of 3 % SDS, 2 % PVA, 2 % Span® 80 and 3 % resorcinol were added to the reactor and added also PEG water mixture. Then again it was stirred at 500 rpm for 25 min, 25 g of urea was added that time and 2 % ammonium chloride was added. Thus, oil-in-water system is formed and colloidal dispersion solution containing phase change material is formed. Then stirring speed reduced to 300 rpm and pH is lowered to 3.5-4.0 by adding acetic acid [20]. Finally stoichiometric molar amount of 35 % formaldehyde (10 g) is added and the reaction is preceded for 30 min at 30 °C. When finished reaction, the solution is cooled down to 20 °C and then dried in the vacuum over for 12 h to complete removal of free formaldehyde from the microcapsules. Same procedure was done for 5 and 7.5 wt % of PEG-1000. The synthesis of urea-formaldehyde polymer was formed in two steps. At first, by the addition of formaldehyde with amino group of urea, urea is converted into hydroxymethylolated. This reaction is actually a series of reactions that leads to the formation of monomethylolurea, dimethylolurea and trimethylolurea. The second stage of the urea-formaldehyde resin synthesis consists of the condensation of methylolurea to a low molecular weight polymer [21].

TABLE-1
PEG-1000 PROPERTIES

Thermal conductivity (Wm K^{-1})	0.2
Density (kg m^{-3})	750
Specific heat (kJ kg^{-1} K^{-1})	1.5
Latent heat (kJ kg^{-1})	64
Thickness (mm)	4
Melting temperature (°C)	35

Addition of the microcapsules and coating to the fabric: The stock paste was prepared according to materials included acrylic based binder 50 g kg^{-1}, ammonia liquor 10 g kg^{-1} and Thickener (synthetic thickener PTF) 40 g kg^{-1} and microcapsules were also prepared. Then the coating paste was made using 50 g of microcapsules and 50 g of stock paste by electric stirrer. Then it was applied on to the fabric with the help of rubber squeegee. The angle of rubber squeegee was kept at 75 °C. The paste was applied in the form of two layers. After the application, the samples were dried at 110 °C. A total of six samples were cured for three wt (%) of PEG-1000 at the following time 1-2.5 min and temperatures ranges are (140, 155 and 170) °C is shown in Table-2.

Characterization of the microcapsules: The functional groups in the PEG micro capsulated samples were obtained with a Bruker (Tensor 27) Fourier transform infrared spectrophotometer (FT-IR) in the range between 4000 and 400 cm^{-1}. A differential scanning colorimetry model (DSC) Q100 of TA Instrument was used to measure the phase change temperatures

TABLE-2
DIFFERENT CONCENTRATIONS (wt %) OF PHASE CHANGE MATERIAL APPLIED ON FABRIC

No. of samples	PEG conc. (%)	No. of samples	PEG conc. (%)	No. of samples	PEG conc. (%)
1		7		13	
2		8		14	
3	2.5	9	5.0	15	7.5
4		10		16	
5		11		17	
6		12		18	

and energy storage capacities of different samples employed and obtained were performed in an equipped with a refrigerated cooling system under an N_2 atmosphere. The samples were heated up to 220 °C at a constant rate 10 °C min^{-1}. Scanning electron microscope measurement of the phase change material microcapsules was carried out on Hitachi-S 3400 N, (Japan). Also, optical microscopy was performed for the observation of the microcapsules in the slurry state. Tensile strength of coated fabric was measured warp-wise by following ASTM-D-5035(1995) method using Instron tensile tester (Model No. 5565). Tearing strength of coated fabric was measured according to the ASTM D2261-13, by the Tongue (Single Rip) procedure. Air permeability was tested according to ASTM standard D737-1996 by Fraizer instrument. The measurements were performed at a constant pressure drop of 196 Pa (20 cm^2 test area). Thermal Resistance of clothing material was measured by using Sweating Hot Plate that was obtained from MTNW Inc. Then the plate was put inside the TPS Lunaire Climatic Chamber. Humidity and temperature of the chamber was maintained at 65 % and 21 °C. This taste was done according to ASTM F 1868-02.

RESULTS AND DISCUSSION

FT-IR analysis: It is clear that a FT-IR spectrum of standard cotton sample is shown in Fig. 2(a). Carboxylic acid radicals exhibit two peaks at 3400-2400 cm^{-1} and 1440-1400 cm^{-1} and near ketones spectra is 1300-1101cm^{-1}. These peaks are attributed to O-H bending's and -C-O stretching vibrations. Then in case of binder coated fabric Fig. 2(b) spectra showed for carboxylic acid radicals peaks at 3400-2400 cm^{-1} and for aldehydes peaks at 2850-2750 cm^{-1} and for anhydrides spectra at 1300-900 cm^{-1}. These peaks are attributed to O-H, -C-O and C-H aldehyde stretching vibrations. The spectrum of the urea-formaldehyde 2.5 % PEG microcapsule is shown in Fig. 2(c)

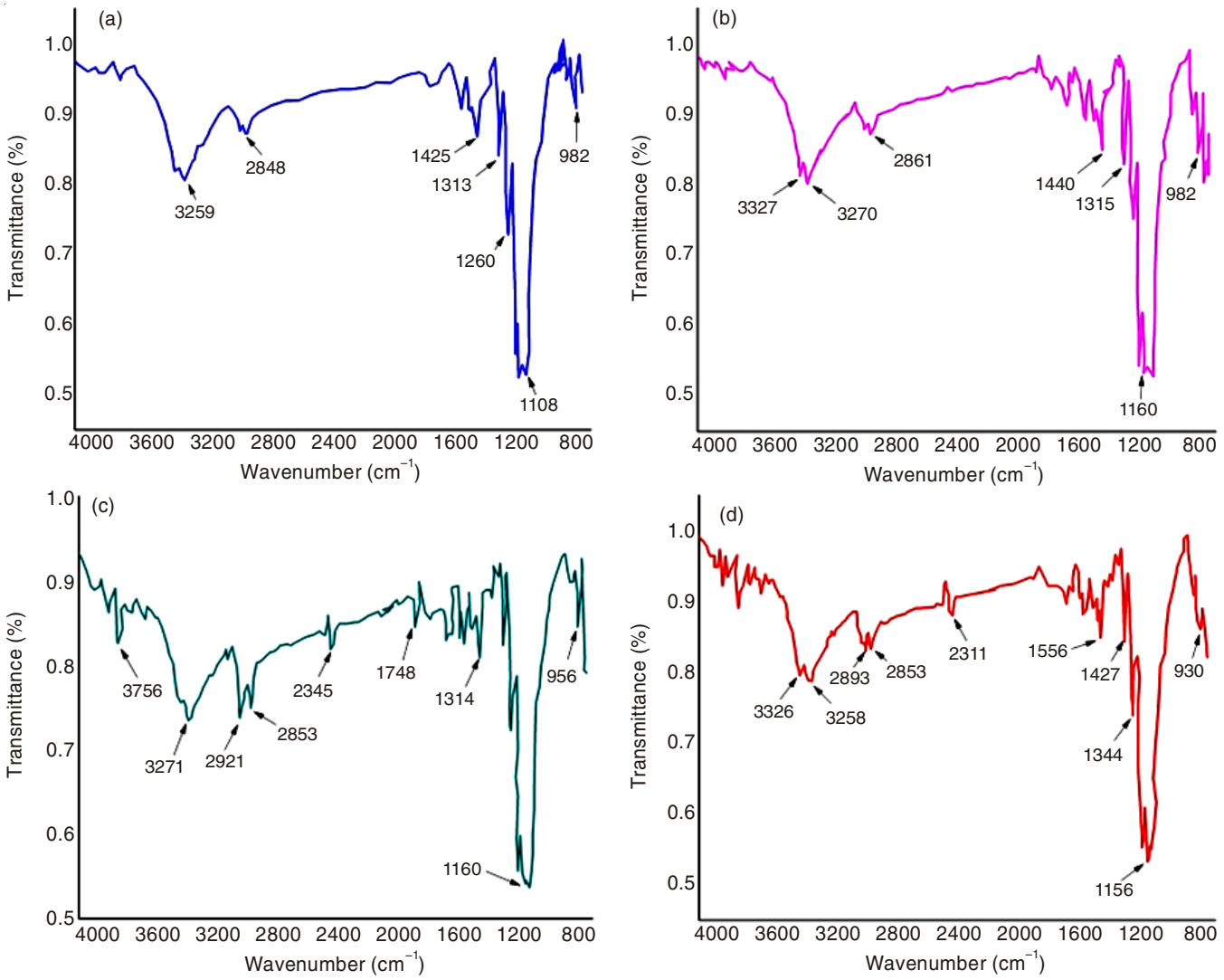

Fig. 2. FT-IR spectra of (a) cotton (b) cotton with binder (c) cotton with 2.5 % PEG (d) cotton with 5 % PEG

demonstrating expected peaks 1200-800 cm^{-1} region and around 3400-2400 cm^{-1} show the presence of alcohols and ethers functional groups of polyethylene glycol. These peaks are attributed to O-H stretch, O-H and C-O-C (dialkyl) stretching vibrations. Then the spectrum of the urea-formaldehyde 5 % PEG microcapsule is shown in Fig. 2(d) demonstrating expected peaks at 3500-3300 cm^{-1} attributed to the presence of amino-groups, 3400-3300 cm^{-1}, attributed to the presence of alcohols and 1300-1000 cm^{-1} ethers functional groups of polyethylene glycol. These peaks are attributed to N-H stretch (1 per N-H bond), O-H and C-O-C (dialkyl) stretching vibrations.

By using 7.5 % PEG-1000 we did not get any significant changes comparison with 5 % PEG-1000.

Differential scanning colorimetry (DSC) model analysis: The results are shown in Fig. 3(a) standard cotton sample exhibits negligible exothermic effect of adsorption due to a small amount of moisture present in the adsorbent. The sensible heat energy storage capacity of cotton was 1.33 kJ g^{-1}. Analysis for binder coated fabric Fig. 3(b) showed that the heat storage capacity of the coated fabric with binder was 1.55 kJ g^{-1} in the range from 40 to 130 °C and the phase change temperature (T_m) of the microcapsules was found to be around 77.9 °C. Thus, cotton coated fabric shows an endothermic behaviour in the specified range of temperature. Phase change temperature T_m of the microcapsules for 2.5 % PEG coated fabric Fig. 3(c) was found to be around 92.8 °C. The heat storage capacity of the microcapsule was 2.84 kJ g^{-1}. Then, phase change temperature T_m of the microcapsules for 5 % PEG coated fabric Fig. 3(d) was found to be around 95.1 °C. The heat storage capacity of the microcapsule was 3.96 kJ g^{-1}. Heat analysis of 7.5 % PEG coated fabric Fig. 3(e) shows phase change temperature T_m of the microcapsules was found to be around 82.1 °C. The heat storage capacity of the microcapsule was 1.57 kJ g^{-1}. The results of DSC analysis show that, when the phase change material microcapsules are heated, they absorb energy and go from a solid state to a liquid state. This phase change produces a temporary cooling effect in the clothing layer. If the phase change material microcapsules are cooled down below the freezing point of phase change material, the material will change back to solid state from the liquid state, releasing heat and thus developing a temporary warming effect. Near 30 °C the recrystallization of the phase change material can causing the exothermic reaction, thus releasing heat to the fabric. This phenomenon is helpful to the wearer of the fabric in winter because it provides him body comfort. In addition, presence of free alcoholic or carboxyl groups in the phase change material composite materials causes high latent heat storage. It is worth noting, that carboxyl group give more latent heat than alcoholic group.

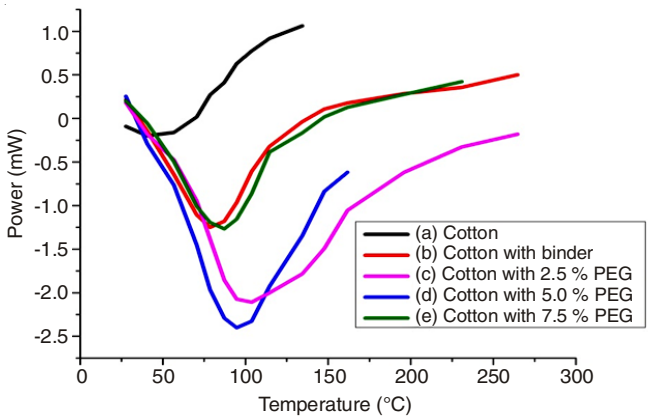

Fig. 3. DSC analysis of (a) cotton (b) cotton with binder (c) cotton with 2.5 % PEG (d) cotton with 5 % PEG and (e) cotton with 7.5 % PEG

It was concluded that the maximum amount of thermal energy was storage by the fabric coated with microcapsules having 5 wt % of phase change material Table-3. This phenomenon is helpful to the wearer of the fabric in winter because it provides body comfort.

TABLE-3
THERMAL ENERGY STORAGE

Samples	Temperature range (°C)	Thermal energy storage (kJ g^{-1})
Cotton	Not available	1.33
Cotton with binder	30-140	1.55
Cotton with 2.5 % PEG	30-140	2.84
Cotton with 5.0 % PEG	30-140	3.96
Cotton with 7.5 % PEG	30-140	1.57

Morphological analysis: Fig. 4(a) shows that microcapsules of PEG are clearly observed with a microscope of higher resolution (CZM6) microscope. SEM images on Fig. 4(b) demonstrate that microcapsules have spherical shape with average diameter of 25 μm. From Fig. 4(c) it implies that a homogeneous distribution of spherical particles deposited on the surface of the untreated cotton fiber. When fiber is treated with binder Fig. 4(d) the very smooth appearances can be found. Fig. 4(e) Cotton treated with microcapsules shows that the particle of the phase change materials which are reacted with cotton. The microcapsules are located at interstices between the fibers and on the fiber surface. In this case, phase change material is interacting chemically bonded through the hydroxyl groups that make it stable to washing process.

Thermal resistance properties and air permeability testing: Thermal resistance and air permeability of textile material are characterizing their comfort to the wearer. The results are provided in the Table-4. The results demonstrate that 15 % increase in thermal resistance of the fabric sample coated with microcapsules. Evidently, during the testing experiment phase change material microcapsules absorb heat from sweating hot plate that resulted in reducing apparent heat transfer through the fabric. Due to this phase transfer phenomena microcapsules are playing a vital role in resisting the heat transfer and regulating the body temperature.

Testing results of air permeability are also shown in the Table-4. This parameter is significantly reduced due to the

TABLE-4
DATA OF THERMAL RESISTANCE AND
AIR PERMEABILITY TESTING

Types of samples	Air permeability ($cm^3\ cm^{-2}\ s^{-1}$)	Thermal resistance ($Km^2\ W^{-1}$)
Cotton	85.33	0.0352
Coated with binder	82.43	0.0362
Coated with 2.5 % PEG	66.96	0.0405
Coated with 5.0 % PEG	61.61	0.0420
Coated with 7.5 % PEG	54.67	0.0441

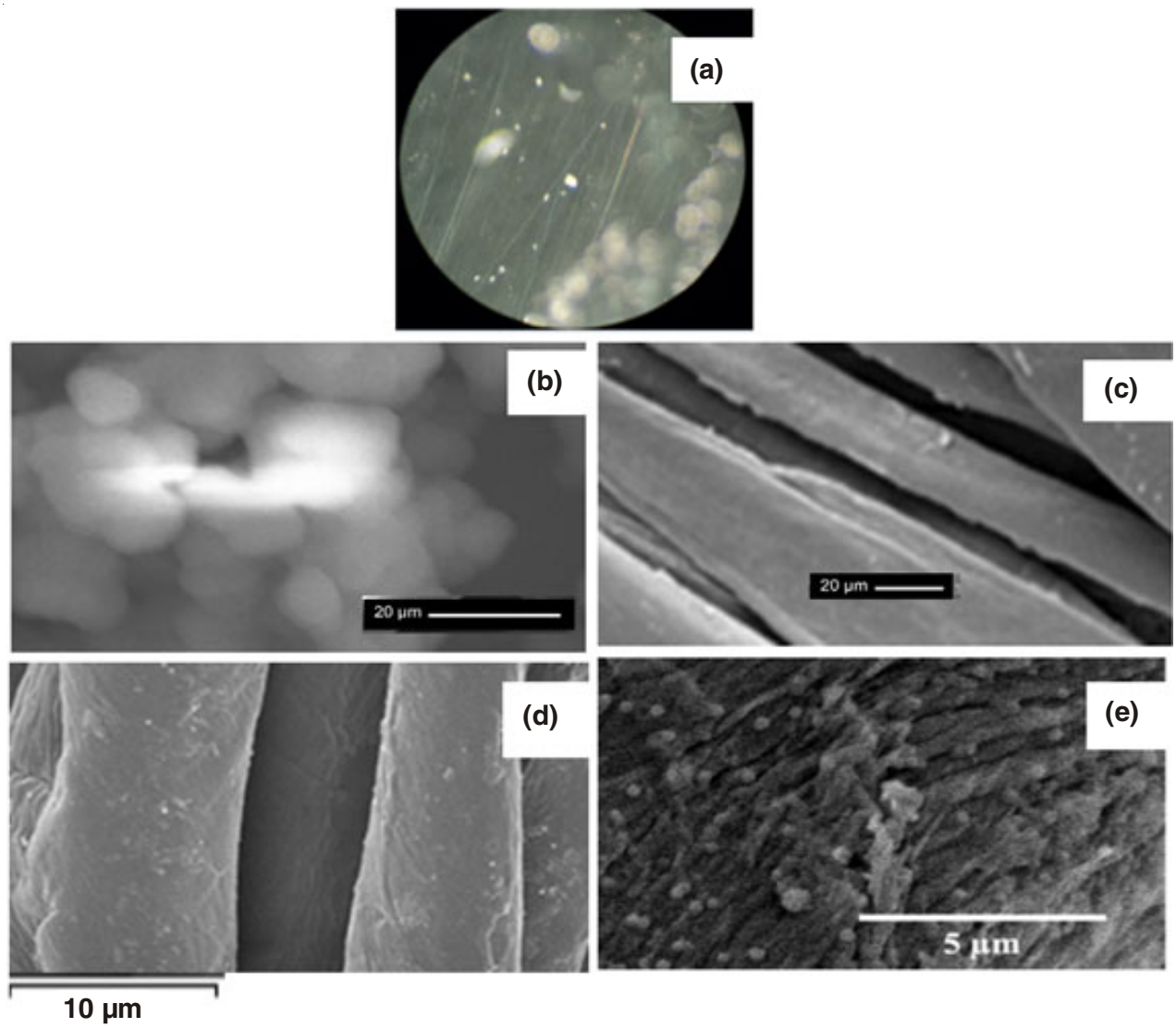

Fig. 4. (a) Optical microscopy image of the microcapsules; SEM image (b) microcapsules (c) untreated cotton fiber, (d) treated with binder and (e) treated with phase change materials

presence of acrylic binder coating decreasing the average diameter of the open channels for air transport through the fabric. Therefore, thickness of the coating needs to be optimized.

Tensile and tearing strength testing: It can be observed that there is significant change in warp way tensile strength as compared to weft way tensile strength. An increase in warp and weft way strength may be a result of extra bonding between the fibers provided by the acrylic binder coating (Table-5). From the results shown in the Table-6, it can be observed that there is significant decrease in tear strength in weft direction. This may be because of increase in stiffness of the fabric due to the application of coating.

Conclusion

We have proven that the microencapsulation technique presented in this study, based on *in situ* polymerization technique of high molecular weight PEG-1000 and further fixation by the binder on the surface of cotton fabric, changed into quite successful to provide microcapsules with a more desirable thermal ability with regards to the phase change material content. The PEG soft segment phase transition between

TABLE-5
TENSILE STRENGTH TESTING VALUES

Sample No.	Sample type	Warp (N)	Weft (N)
1	Cotton	1059	510
2	Coated with binder	1020	588
3	Coated with 2.5 % PEG	1000	569
4		961	569
5		1039	588
6		961	588
7		882	569
8		1020	627
9	Coated with 5.0 % PEG	824	530
10		942	530
11		971	530
12		981	628
13		1020	588
14		1040	530
15	Coated with 7.5 % PEG	922	628
16		902	588
17		902	588
18		1001	569
19		1020	588
20		1040	608

TABLE-6
TEARING STRENGTH TESTING VALUES

Sample No.	Sample type	Warp (N)	Weft (N)
1	Cotton	24.03	10.20
2	Coated with binder	16.67	8.63
3	Coated with 2.5 % PEG	18.14	8.63
4		18.63	7.74
5		19.62	7.06
6		18.14	7.45
7		23.54	6.96
8		20.60	6.96
9	Coated with 5.0 % PEG	21.09	6.86
10		22.56	7.45
11		20.60	6.37
12		23.54	6.47
13		23.54	7.94
14		23.93	7.84
15	Coated with 7.5 % PEG	21.09	8.24
16		19.62	8.63
17		22.56	8.24
18		23.54	8.63
19		20.40	8.63
20		21.97	8.63

crystalline and amorphous states resulted in heat storage and release of PEG/formaldehyde. At temperature above the PEG phase melting transition, the PEG/formaldehyde was still solid because the hydrogen bonded hard segments restricted the free movement of the soft segments. Properties of microencapsulated PEG were characterized by optical and electronic microscopy, while results of application of different amount of phase change material on cotton fabric were tested by thermal analysis, tensile strength, tearing strength, heat resistance and air permeability of textile material. The differential scanning calorimetry results indicated that 5 % PEG on cotton fabric provides satisfied results for thermal energy storage, 3.96 kJ g^{-1}. It is clear that the ultimate strength and ultimate air permeability results of all the composites are lower than raw cotton. Since there were many interspaces among the fibers in the testing fibril, the cross-section area of the fibril measured by a micrometer was not equal exactly to the real cross-section area of the fibers. Therefore, the collected data is semi quantitative to a certain extent. However, the PEG composite materials with reliable thermal properties are suitable and promising in serving as phase change materials for thermal energy storage and temperature regulation. Moreover, polymeric microcapsules as phase changing material provide increased thermal resistance of the fabric and potential of self-regulating properties for human skin and thermal sensation.

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