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A Review on Application of Phase Change Materials in Textiles Finishing

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***Abstract*—**Fabric as the first and most common layer that is in permanent contact with human skin is a very good interface to provide coverage, as well as heat and cold insulation. Phase change materials (PCMs) are organic and inorganic compounds which have the capability of absorbing and releasing noticeable amounts of latent heat during phase transitions between solid and liquid phases at a low temperature range. PCMs come across phase changes (liquid-solid and solid-liquid transitions) during absorbing and releasing thermal heat; so, in order to use them for a long time, they should have been encapsulated in polymeric shells, so-called microcapsules. Microencapsulation and nanoencapsulation methods have been developed in order to reduce the reactivity of a PCM with outside environment, promoting the ease of handling, decreasing the diffusion and evaporation rates. Methods of incorporation of PCMs in textiles such as electrospinning and determining thermal properties had been summarized. Paraffin waxes catch a lot of attention due to their high thermal storage density, repeatability of phase change, thermal stability, small volume change during phase transition, chemical stability, non-toxicity, non-flammability, non-corrosive and low cost and they seem to play a key role in confronting with climate change and global warming. In this article, we aimed to review the researches concentrating on the characteristics of PCMs and new materials and methods of microencapsulation.

***Keywords*—**Thermoregulation, phase change materials, microencapsulation, thermal energy storage, nanoencapsulation.

I. Introduction

BY changing the temperature of different parts of the body, as well as the environment temperature, textiles containing PCMs get affected and react proportional to the temperature of the ambient. Due to change of the physical state of PCMs (liquid-solid, solid-solid) in terms of different thermal conditions, application of the microencapsulation technique is necessary and requisite for preserve, protect and optimal use of PCM. The main role of the clothing is to protect the body from various thermal fluctuations and therefore use of microcapsules containing PCM (micro PCM) in manufacturing and finishing processes of textiles will significantly improve and enhance their thermoregulating property. Microencapsulated phase change materials (mPCMs) during absorbing and storing thermal energy and releasing of it come across solid-liquid and liquid-solid transitions, respectively. The mentioned process is called phase transition (phase change). PCMs store thermal energy during heating process and they release the previously stored thermal energy during cooling process and therefore they are widely being applied in manufacturing and finishing of various textiles. They can be directly applied within fibers (acrylic fiber) and foams (polyurethane foam) or as a lining in production of various fabrics. Naturally, the body has the ability of adapting itself with surrounding temperature changes in different climatic conditions. The majority of this adaptation is done by the skin, although abnormal thermal fluctuations can be fatal as actions such as shaking, horripilation, mouth and nose secretions, severe sweating and too much breathing are not able to cause automatic thermoregulation and performing intense physical exercise, application of proper clothing and artificial heating and cooling are inevitable for maintaining thermal equilibrium [1]. The technology of embedding PCMs inside fabric structure in order to enhance their thermal properties in the late 1980s had been taken under account via NASA's development program. At the beginning, the main goal of applying this technology was astronauts' space suits in order to provide higher protection against high thermal fluctuations in outer space [2]. PCMs were embedded into textile materials with the development of microencapsulation technologies in 1987. Currently, more than 500 PCMs are known which were embedded directly inside fibers either foams or applied topically. Among the various PCMs, paraffin waxes (n-paraffin) with a melting point between 18°C and 36°C can be mentioned (heptadecane, hexadecane, octadecane, nonadecane and eicosane). Paraffin waxes, according to the number of carbon atoms in their chemical structure, have various melting and crystallization temperatures. Paraffin waxes cannot be directly embedded into textiles as their melting point is low, so in order to embed them inside textiles, microencapsulation is inevitable. We can encapsulate PCMs inside fine polymeric flexible layers (microcapsules) via microencapsulation technique in which they can easily change from solid to liquid phase and vice versa [1].

II. Researches and Studies in Relation to Application of PCMs in Textiles Finishing

Right now manufacturing heat storing and thermoregulating textiles and clothing include the following methods: electrospinning of fibers via various PCMs, addition of micro PCMs to fibers, textiles and foams and direct addition of PCMs to textiles, fibers and foams.

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A. Electrospinning of Fibers via Various PCMs

A wide variety of thermoregulating fibers could not be manufactured via conventional spinning methods as the processability of many polymers and PCMs is difficult. The application of electrospinning is one of the proper and optimal methods of manufacturing thermoregulating fibers. In order to produce large quantities of ultra-fine fibers in micro and nanoscale containing a variety of polymers (polymeric mixtures and polymer impregnated with nanoparticles), electrospinning is a very simple, easy and flexible method. In electrospinning process (Fig. 1), mainly polymeric solutions are being applied. In order to manufacture nanofibers with a full range of composition, a variety of morphologies and properties, composites, surfactant based solutions and sol-gels are also used [3].

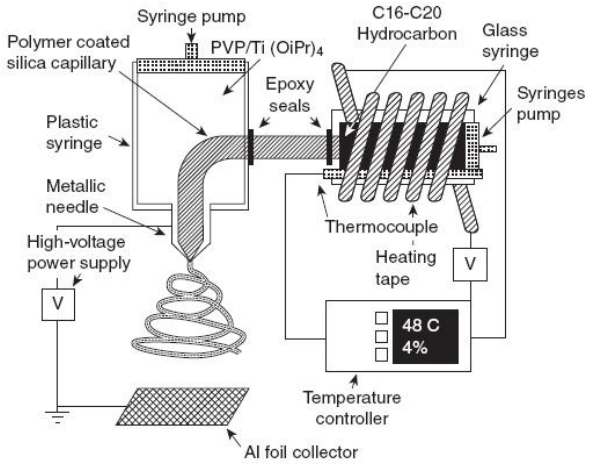

Fig. 1 Manufacturing of TiO_2-PVP nanofibers loaded with PCMs via melt coaxial electrospinning [4]

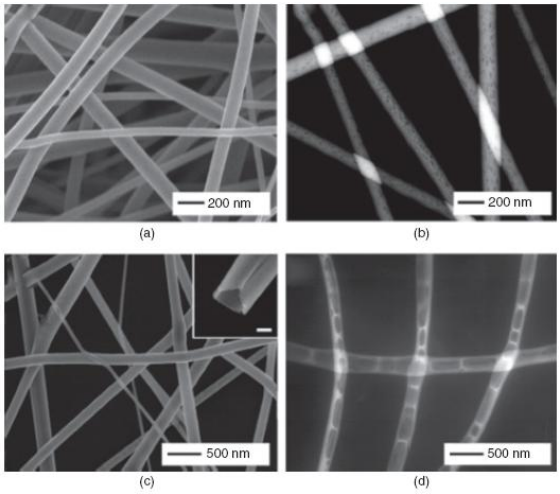

Fig. 2 Octadecane @ TiO_2-PVP nanofibers obtained via melt coaxial electrospinning with spinneret: (a) SEM micrograph of nanofibers with 7% octadecane, (b) TEM of nanofibers after removal of octadecane, (c) SEM micrograph of nanofibers with 45% octadecane and (d) TEM of nanofibers and octadecane removal [4]

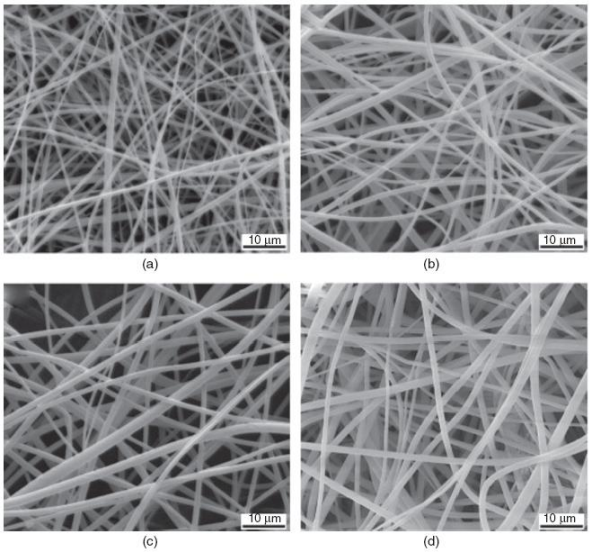

Fig. 3 Electrospun fibers SEM micrographs: (a) CA fibers, (b) PEG/CA fibers, (c) washed PEG/CA fibers and (d) PEG/CA fibers after 100 heating and cooling cycles [5]

Melt coaxial electrospinning method for manufacturing phase change nanofibers consisted of n-octadecane and n-eicosane cores and composite polymeric shells had been developed in one step [4]. In the mentioned process, n-octadecane PCM was removed by impregnation in hexane for 24 hours. Obtained TiO_2-PVP (polyvinylpyrrolidone) nanoparticles due to the rapid freezing of hydrocarbons obtained from the cooling of the carrier solution's vapor, displayed novel segmentized morphologies. N-hexadecane-PVP, n-octadecane-PVP and n-eicosane-PVP nanofibers enthalpy changes at 16°C, 27°C and 37°C were 71 KJ/KG, 114 KJ/KG and 88 KJ/KG, respectively (Fig. 2).

Taking advantage of the electrospinning method, PEG 10000 and cellulose acetate (CA) ultrafine fibers were prepared [5]. Based on the results of the mentioned research, maximum PEG content in fibers with ΔH_{fus} of 86 KJ/Kg at 58.5°C and ΔH_{cryst} of 65.2 KJ/Kg at 39°C, could reach 70 wt% (Fig. 3).

In the context of fibers manufactured via electrospinning, fibers were constructed by using polyvinylidene fluoride (PVDF) and PEG 1000 mixtures with various PEG 1000 contents. According to the obtained results, the diameter of the electrospun fibers is in direct relation with the PEG 1000 content of the compound. Some of the obtained results are as: 1-PVDF/PEG 1000 mats containing silica, represented good mechanical strength and high values of thermal capacities between 59.2 KJ/Kg and 72.2 KJ/Kg at 38.5°C. A variety of mentioned mats could have various applications in energy storage and the manufacture of thermoregulating fibers [6]. LA/PET (1:1, w/w) ultrafine fibers manufactured via electrospinning method. Fibers had average diameter of 710 nm and they were cylindrical in shape and had smooth surface. Fibers phase change temperatures were 45.1°C and 38.6°C and the corresponding enthalpy changes was 70.8 KJ/Kg and 62.1

KJ/Kg, respectively [7], [8]. Ultrafine fibers were electrospun through stearyl stearate (SS) and polyethylene terephthalate (PET). According to the obtained results, thermal capacities of SS/PET fibers with 10/100-50/100 at 50 °C, increased from 14.3 to 53.8 KJ/Kg [9]. Ultrafine fibers consisted of PET, LA and silica nanoparticles manufactured via electrospinning [10]. In another study, a series of diacid dioctadecyl esters (DADOE) had been synthesized, and subsequently, DADOE fibers with PET were obtained. From the obtained results it was concluded that when the DADOE content of DADOE/PET fibers was less than 50%, the obtained fibers had smooth surface, good morphology and average diameter of fiber increased from 375 nm (pure PET fiber) to more than 1 μm as a result of DADOE content increase. Subsequent heating cycles, DADOE/PET fibers had the thermal stability and capacity of 65 KJ/Kg at 45-48°C [11].

B. Addition of MicroPCMs to Fibers, Textiles and Foams

New and novel methods had been developed in order to add and embed microPCMs to textiles. Researchers by applying new techniques had been able to solve the problem of adding enough PCM inside the fiber structure and improve thermal properties and simultaneous maintaining mechanical properties of fibers. In performed researches, microcapsules containing PCMs impregnated in a binder, subsequently fibers and textiles coated by binder mixture and by applying microPCMs, two and more layers of polymeric foams as thermal insulation pads for shoe insoles had been investigated [12]-[15]. Various textiles applications had been developed after the mentioned researches such as follows: flexible fit clothing for diving in cold water [16], leather products impregnated by microPCMs [17]-[19], textile layers with formed canals filled by microPCMs [20], firefighter clothing, diving, hard work garment, military coveralls, gloves and special shoes [21], [22] and special textiles products containing thermoelectric circuits printed by microPCMs [23]. Initial investigations regarding the manufacturing of foams containing microencapsulated n-alkanes (13-27 C) was conducted and discussed by researchers. In these studies, 20-60 wt% microPCMs added and mixed to a prepolymer compound before hardening in order to ensure homogeneous distribution in the entire system. The manufactured composite foam was considered appropriate for the application as gloves lining, shoes, outdoor wear, car upholstery and medical products [13]. Thermal performance of commercial insulation foams including microPCMs in clothing system had been studied and analytical method obtained for comparison of relative thermal properties of dry garments containing PCM and commercially available dry fabric. Based on the results of this study, it was defined that dry fabrics containing microPCMs could reduce the heat loss of divers during the first phase of diving [24]. In order to investigate the impact of microPCMs on heat and humidity conductivity in textiles, single and double layer textile laminated by PU foam containing 60 wt% of n-octadecane and n-hexadecane microcapsules was manufactured [25]. Other researchers manufactured polyurethane foam incorporated by 12.6 wt% microencapsulated n-octadecane (Fig. 4). Thermal capacity of the foam was measured 12 KJ/Kg between 28°C and 31°C [26].

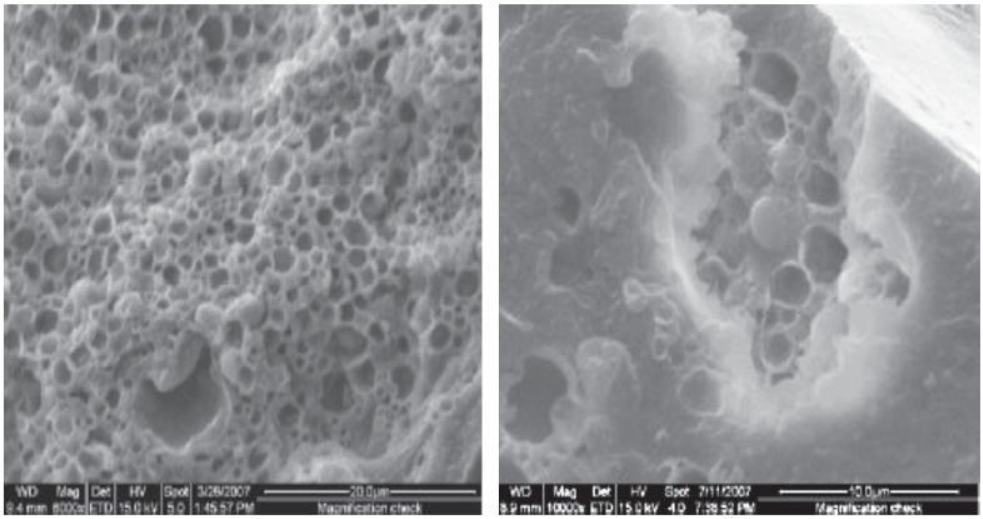

Fig. 4 SEM micrographs of microPCMs/polyurethane composite foam: (a) × 6000 and (b) × 10000 [26]

Soft polyurethane (PU) foams containing 23.6-25.4 wt% n-octadecane, n-nonadecane and n-eicosane microcapsules with styrene-divinylbenzene copolymer shell were manufactured by researchers and the enthalpy of foam containing 25.2% microencapsulated n-octadecane was measured 28 KJ/Kg [27], [28].

C. Direct Addition of PCMs to Textiles, Fibers and Foams

Polyester, cotton, polyamide 66 and wool textiles were

prepared by PEG 600, PEG 1000, 2,2-dimethyl-1,3-propanediol, 2 hydroxymethyl 1-2 methyl 1,3 propanediol aqueous solutions. In comparison to untreated textiles, they had 250% more thermal storage and releasing capacities. Thermal properties of optimized textiles remained stable even after 50 heating and cooling cycles [29]. Also first commercial phase change textile named Neurtratherm® manufactured and introduced by coating with PEG 1000. The phase change property of the manufactured fabric only lasted 20 minutes. Researchers reported that with providing a cross-link on the textiles by PEGs (molecular weight 600-1000) via a reaction by dimethylol dihydroxyethyleneurea under conventional pad-dry-cure conditions, stability of the thermoregulating property could be enhanced. Also, according to the announced results, the manufactured textiles retained their thermoregulating property even after laundering [30]. Fibrous layers (cellulose, polyolefin and fibers mixture) with different structure were studied by PEGs solution (molecular weight = 1000, 1450) containing DMDHEU and a catalyst acid mixture. The researchers found that the textiles thermal properties in proportion to the degree of cross-linking in amorphous and crystalline areas of semi-crystalline PEGs attached to the fibrous layers, is different [31]. Cotton, cotton/polyester and wool textiles designed with heating and cooling effects via a coating on their surfaces by PEG 1000 and PEG 1450 and PEG 600-PEG1000 were added to cotton/polyester textiles by Knife-over-blanket in an experimental printing machine. The applied coating material was a urethane-based synthetic disperse of breathable foam with fine pores containing 45-48% active material. In order to increase the degree of cross-linking, a water miscible non-ionic stabilizing agent was applied. Stabilization operations of coated samples containing 17% PCM performed in an oven for 15 minutes at 60-80°C. According to obtained results between 1°C and 34°C temperature ranges, textiles containing PEG 600-PEG 1000 stored and released 22 KJ/Kg heat [32] (Fig. 5).

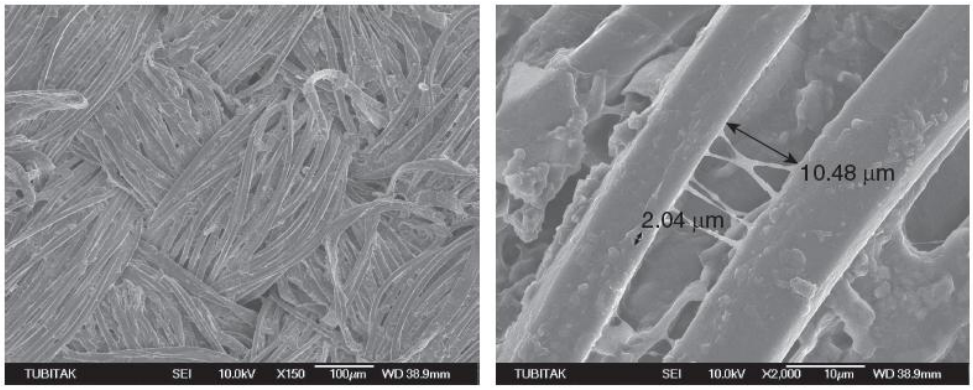

Fig. 5 SEM micrograph of fabric finished by PCM [32]

Polylactic acid (PLA) was invented and in commercial applications of textiles is growing in interest day-by-day [33]. The effect of PEG coating on thermoregulating, antistatic, air permeability, and mechanical properties of PLA textile was investigated. In order to obtain supersaturated PEG 1500 with acceptable stability characteristics by crosslink with DMDHEU, PEG 1500 was fixed on the surface of PLA textile at temperature lower than PLA melting point. After three washing cycles, heat absorbed by PLA textile with 50 wt% PEG was 35 KJ/Kg between 39°C and 56°C [34]. Other researchers widely used PEGs for direct addition to fiber or textile matrix. Although mentioned materials are directly being added to textiles, they are not desirable for applications requiring textile dry cleaning. Studies regarding the application of PEGs for textiles were largely focused on attaching PEGs to textiles, which is related to PEG molecular weight, crosslinking agent and catalyst concentration, curing conditions and fiber polymer type. In addition to obtained thermal characteristics, by application of PEG, textiles resistance against abrasion and pilling also improves [35]. Other researchers became pioneers in the direct addition of PEGs to fibers in order to improve thermoregulating textiles [29], [36]. Composite fibers from PEG with polypropylene (PP), polyethylene terephthalate (PET), or ethylene-vinyl acetate were prepared via physical mixing by controlling the spinning parameters and components [37]. PET copolymerized by various molecular weight PEGs (300, 600, 1000, 2000, 4000 and 6000) and the fibers were melt spun from the copolymer. When the compound included 45 wt% of PEG4000-PEG6000, the enthalpy for fibers measured 26.9 KJ/Kg between 19.6°C and 49.3°C [38]. Thermoregulating fiber (PEG based shape memory thermoplastic polyurethane) obtained from the mentioned experiment at temperatures above PEG melting point still had a certain mechanical strength, because the hydrogen bonded hard, the segment which reacts as a physical crosslink limited the free movement of PEG soft segment. The mentioned fiber had thermal capacity of 100 KJ/Kg at 44.7 °C [39]. Other researchers have added PEG inside wool fiber and investigated the effect of surface energy and charge of wool fiber in order to obtain a high amount of cross-linked PEG with acceptable stability characteristics. These researchers impregnated chlorinated, fluorinated and untreated wool fabrics in 50% PEG 1000 bath. Padded textiles were dried for 5 minutes at 85°C and then

cured at 120°C for 2 minutes. The samples were washed by 1% phosphate based detergent at 60°C for 10 minutes and subsequently soaked in water for 5 minutes at 25°C and dried later. The thermal capacity of fluorinated textiles between 31.8°C and 47.1°C was 18 KJ/Kg and for chlorinated textiles, it was 10 KJ/Kg between 30.8°C and 43.2°C [40]. Multicomponent fiber consisted of paraffin waxes such as n-octadecane, n-nonadecane, n-eicosane, n-heneicosane or their mixtures with melting points between 20°C and 50°C had been developed in fiber core by melt spinning. In performed researchers fiber forming polymers were consisted of polyesters, polyamides, polycarbonates, polyoxymethylenes and polyacrylates, because these polymers did not solve at temperatures above PCMs melting or softening points, and therefore, prevent PCM materials leakage. Multicomponent fibers had thermal capacities of 20-40 KJ/Kg between 0°C and 50°C. Based on the obtained results from the mentioned experiments, multicomponent thermoregulating fibers could be used by other types of fibers such as synthetic fibers, cotton, wool or viscose [41]. Additional research in this field was continued by other researchers and based on performed researches, it was found that HDPE with high molecular weight was a suitable viscosity modifier for paraffin waxes and fibers containing 15-42 wt% n-octadecane had thermal capacities of 26 KJ/Kg and 86 KJ/Kg and tenacity of 33 CN/Tex to 16 CN/Tex [42].

III. Conclusion

Customer satisfaction, novel products manufacturing and ensuring a fair income is desired for textiles industry producers and activists, such as other industrial fields, and therefore, manufacturing textiles containing PCMs, textiles which are capable of absorbing, storing and gradual releasing of thermal heat, had been taken under account even more than before. According to the results of the performed researches regarding PCMs and the way of applying them to textiles, electrospinning fibers by use of these materials and the application of microencapsulated PCMs to textiles had priority in comparison to their direct incorporation to textiles and foams. Since PCM materials change phase (solid-liquid, liquid-solid) with thermal fluctuations, therefore in order to save, stabilize and optimal use of them, microencapsulation method inside a flexible polymeric shell and also electrospinning fibers with these materials is recommended. Since the phase change amplitude of the PCMs is very different, so in the textiles industry, the application of PCMs according to body temperature changes will be preferred. The application of PCMs in textiles improves their thermal efficiency and is an effective action in improving the quality of fabrics consumed by humans. In order to provide balance in body temperature, especially in cold environments, it is inevitable to increase the ambient thermal energy consumption or put on more clothes; therefore generally, the application of PCMs in the textile industry causes the related costs to reduce provide economic savings for consumers. By the use of PCMs due to their repeatability of phase change and reduction of human need to supply thermal energy from fossil fuels, it can be stated that these materials have positive effects on the environment.

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