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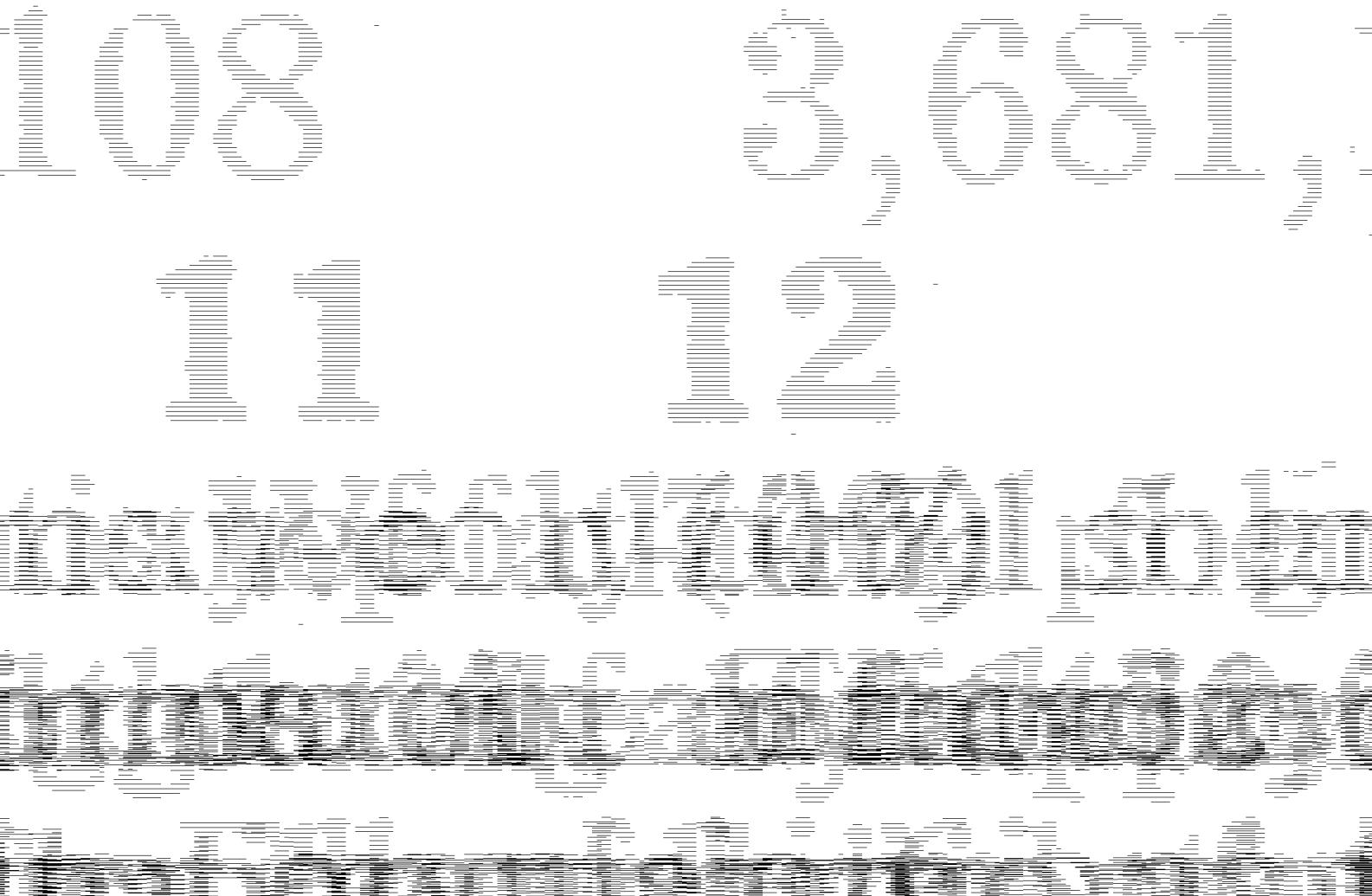
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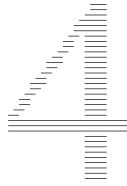
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# Development of thermo-regulating fabric using phase change material (PCM)

Prasad S. Bhatkhande

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Development of Thermo-regulating Fabric Using Phase Change Material (PCM)

by

Prasad S. Bhatkhande

Thesis

Submitted to School of Technology Studies

Eastern Michigan University

In partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

in

Apparel, Textile and Merchandising

Thesis Committee:

Dr. Subhas Ghosh, Chair

Prof. John Boyless

Dr. Vijay Mannari

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I thank the department of polymers and coating for their permission to use SEM and other instruments.

## ABSTRACT

This research study concentrates on use of phase change material (PCM) in textiles which can produce thermo-regulating characteristics to control body temperature useful for various daily wear and technical textiles. The latent heat which is released or absorbed during the process of phase change is studied and discussed in this research. The PCMs are encapsulated into tiny microcapsules to protect from washing out or abrasion. These microcapsules are bounded onto the fabric surface by using a binder. The microcapsules and their effectiveness are tested by using SEM, Optical Microscope, DSC and Comfort tester. The testing is further extended to the physical and chemical property testing to ensure the performance properties of the textile fabric. The research concludes that Polyethylene Glycol is a good phase change material which can be applied to fabric by using a Polyurethane vehicle to produce ultimate bodywear.

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## CHAPTER 1: INTRODUCTION

According to the dictionary, the definition of comfort is a condition or feeling of pleasurable ease, well-being, and contentment. In simpler terms, comfort is sometimes defined as the absence of discomfort. In the context of textiles and clothing, wear comfort is probably a state when we are unaware of the clothing we are wearing. Comfort may be classified into four main categories: thermal or thermo physiological comfort, sensorial comfort, garment fit, and psychological comfort (O'Mahony, & Braddock, 2002). Thermal factor is the most decisive one affecting the comfort level (Jun, Park, Shim, & Kang, 2009). My study deals mainly with the thermal comfort, which is the case when we are feeling neither too cold nor too warm but just right.

Fundamental principles of science are now increasingly employed for the manufacturing of innovative textile products. One such principle is “Phase Change,” the process of going from one physical state to another, i.e. from a solid to a liquid and vice versa. Fiber and textile which have automatic acclimatizing properties are recently attracting more and more attention (Modal, 2008).

Substances that undergo the process of phase change are better known as Phase Change Materials (PCM). They give off heat as they change to a solid state and absorb as they return to a liquid state (Vijayaraaghavan & Gopalakrishnan, 2006). Thermal energy storage (TES) is the temporary storage of high or low temperature energy for later use. It bridges the time gap between energy requirements and energy use. 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 (Modal, 2008).

Phase change materials (PCMs) have been applied to the textiles in a variety of processes to improve thermal comfort of end-use products due to their high heat storage capacities. Coating, lamination, finishing, melt spinning, bi-component synthetic fiber extrusion, injection molding, and foam manufacturing are some of the convenient processes for PCMs' incorporation into the structure. Microcapsule production may be achieved by means of physical or chemical techniques. The use of some techniques has been limited by the high cost of processing, regulatory affairs, and the use of organic solvents, which are a concern for health and the environment. Physical methods are mainly spray drying or centrifugal and fluidized bed processes, which are inherently incapable of producing microcapsules smaller than 100 µm (Modal, 2008).

In situ polymerization generally involves bringing together two immiscible liquids, such as water and organic solvent, containing complimentary, direct-acting, organic intermediates that will react with each other to establish a solid pre-condensate (Brown, Kessler, Sottos, & White, 2003). In this study I have aimed to establish a manufacturing technique based on in situ polymerization in order to accomplish the microencapsulation of PCMs that can ultimately be used in different textile applications.

A comparison of effectiveness of the finish on thermal regulatory property and other physical properties with the untreated sample will support beneficiary to evaluate its work life.

## Purpose of the Study

The overall goal of this investigation is to develop a thermo-regulating fabric that can be used to produce comfortable garments. This study will also evaluate a good PCM material among three different molecular weights of Polyethylene glycol, PEG  $\overline{M}_w$ 600, PEG  $\overline{M}_w$ 1000 and PEG  $\overline{M}_w$  3400.

Based on this goal, following specific objects emerged:

- PCM like PEG will be encapsulated following a polymer synthesis.
- PEG, having three different molecular weights, PEG  $\overline{M}_w$ 600, PEG  $\overline{M}_w$ 1000 and PEG  $\overline{M}_w$ 3400, will be investigated for their thermal behavior.
- The encapsulated PEG microcapsules will be applied onto the textile fabric using poly urethane as coating agent.
- Materials would be tested on DSC for effectiveness of the altered thermal behavior of the fabric.

## Justification and Significance

From original applications in space suits and gloves, phase change materials (PCM) are now used in consumer products. Microencapsulation of liquids and solids is an innovative micro-packing technology which is opening up new marketing opportunities for performance apparel and markets for making smart thermo-regulated textiles. Application range extends from the highly complex life support systems to the convenient and fun, and from lifesaving military uniforms to entertainment. The main areas of focus for smart and interactive textiles are military clothing, healthcare, and performance sportswear. Definitely, PCM incorporated textiles would take a major role in future smart textiles segment. In today's competitive market, the demand of

today's customer is to get comfort in fabric, which is to be worn in different situations from daily wear to a functional wear. Phase change materials are the sources to be incorporated in textile materials to add value that is comfort to wearer (Modal, 2008).

### Hypothesis

The hypothesis of this investigation is that, when PCM material change phases it either gives out or absorbs heat. By using this phenomenon, a PCM material coated fabric can be used for thermal regulation under certain environmental conditions.

### Methodology

Methodology will be described in detail in Chapter 4.

Study design: This study will compare the difference between the thermal properties of a normal cotton fabric and a fabric having a coating of PCM microcapsules.

Experiment procedure: This experiment at work concerns with the in situ polymerization of urea-formaldehyde resins encapsulating the core PEG material. The encapsulated microcapsules are then washed repeatedly and finally vacuum dried to get final microcapsules.

Study type: The best sample bath of polymerization will be the one that shows higher peaks on the DSC, which indicates more heat was given out for the thermal regulation. Tests for textile comfort and durability will be conducted to ensure that the application of the PCM microcapsules to the fabrics do not change important physical properties of the fabrics.

Data gathering procedure and instrumentations: Data will be collected from the DSC testing, which will indicate the thermal properties of the fabric. To test the comfort properties of the fabric, evaporative and thermal resistance tests will be performed using a TPS Lunaire controlled

temperature chamber and sweating hotplate. Bending resistance of the fabric will also be tested using Stiffness Tester. Other physical properties will be evaluated by testing the tensile strength, tear strength, thickness, and air permeability.

Measures to insure safety and confidentiality for human or animal subjects: No human subject will be involved in this study. The researcher will insure his safety by carrying out the synthesis under a closed hood with an exhaust, wearing protective goggles, lab coat, and protective gloves during the time of experimentation.

Data Analysis: Data will be studied on the base of the thermo-gram obtained from DSC analysis showing the peaks of heat release. Other physical properties will be compared with the American Society for Testing and Standards (ASTM) standards.

## CHAPTER 2: LITERATURE REVIEW

Scientific advancement made in various fields has undoubtedly increased the quality and value of human life. It should, however, be recognized that the technological developments have also exposed us to greater risks and danger of being affected by unknown physical, chemical, and biological attacks such as bio weapons, fire, chemicals, radiations, and viruses. Fortunately, simple and effective means of protection from most of these hazards are available. Textiles are an integral part of most protective equipment.

Protective clothing is now a major part of textiles classified as technical or industrial textiles. Protective clothing refers to garments and other fabric related items designed to protect the wearer from harsh environmental effects that may result in injuries or death (Scott, 2005).

The goal of the thermoregulation systems is to maintain the core body temperature and the comfort of the wearer in diverse environments. There are two main characteristics that have been observed in fabric materials that provide thermoregulation. The first is breathability; a highly efficient breathable fabric material enables the user to control body temperature and experience physical comfort by controlling heat loss from the system while at the same time removing excessive sweat. The second characteristic is insulation. The fabric must have a good insulation value to control the airspace in the microclimate between the skin and the garment, or between layers (Corberán, Verde, Gil, & Martínez, 2010).

The definition of comfort is a condition or feeling of pleasurable ease, well-being, and contentment. In simpler terms, comfort is sometimes defined as the absence of discomfort. In the context of textiles and clothing, wear comfort is probably a state when we are unaware of the clothing we are wearing. Comfort may be classified into four main categories: thermal or thermo

physiological comfort, sensorial comfort, garment fit, and psychological comfort. This investigation deals mainly with the thermal comfort which is associated with feeling neither too cold nor too warm. The factors affecting thermal comfort are loss or gain of heat by radiation, conduction, and convection, the loss of heat by evaporation of sweat, the physical work being done by the person, and the environment (O'Mahony, & Braddock, 2002). To develop such clothing, fundamental principles of science are now increasingly employed for the manufacturing of innovative textile products. One such principle is ‘Phase Change’, the process of going from one physical state to another i.e. from solid to a liquid and vice versa (Modal, 2008).

### Phase change materials

Substances that undergo the process of phase change are known as Phase Change Materials (PCM). They give off heat as they change to a solid state and absorb as they return to a liquid state (Vijayaraaghavan, Gopalakrishnan, 2006). Recently, as energy crisis is becoming more and more serious, PCMs are increasingly receiving more and more attention. They can be applied conveniently in many fields such as solar energy utilization, waste heat recovery, intelligent air-conditioned buildings, temperature control greenhouses, electric appliances with thermostatic regulator, energy-storage kitchen utensil, insulating clothing, and so on. New fields of applications are rapidly expanding nowadays (Jiang, Ding, & LI, 2002).

The PCM technology was originally developed for NASA to protect astronauts from the extreme temperature fluctuation in space. PCM fabrics are currently available in configurations designed to maintain the thermal comfort during various activity levels and in various ambient temperatures. By adjusting the melting range of the PCMs used in these products, specialty products can be produced for a variety of protective apparel applications (Vijayaraaghavan, &

Gopalakrishnan, 2006). Comparing the heat absorption during the melting process of a phase change material (PCM) with those in normal materials, we find that a much higher amount of heat is absorbed if a PCM melts. A paraffin-PCM, for example, absorbs approximately 200 J/kg·K of heat if it undergoes a melting process (Modal, 2008).

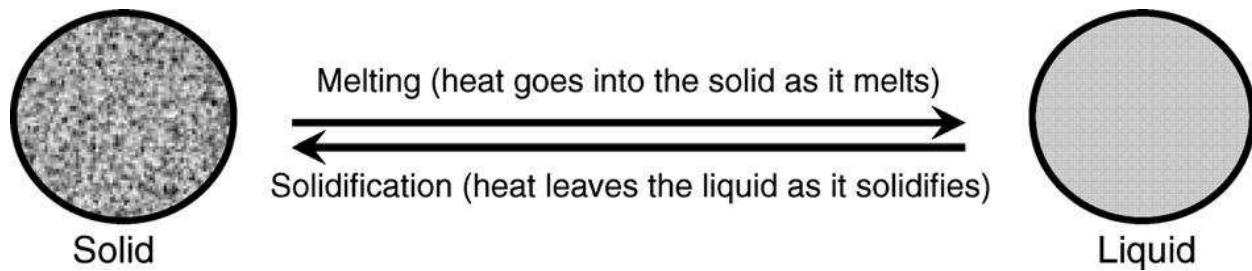


Fig. 2.1. Schematic representation of phase change process

The most common PCMs applied to textiles are n-paraffin waxes with melting temperatures ( $T_m$ 's) of 36–18°C, such as heptadecane, hexadecane, octadecane, nonadecane, and eicosane. They have different phase change temperatures,  $T_m$  and crystallization temperature ( $T_c$ ), which depend on the number of carbons in their structures (Shin, Yoo, & Son, 2005). Energy storage in the walls, ceiling, and floor of buildings may be enhanced by encapsulating suitable phase change materials (PCMs) within these surfaces to capture solar energy directly and increase human comfort by decreasing the frequency of internal air temperature swings and maintaining the temperature closer to the desired temperature for a longer period of time (Khudhair, & Farid, 2004).

In addition to the thermal properties, the air permeability, moisture vapor permeability, and moisture regain of materials also influence the heat balance of the body and, consequently, affect clothing comfort. Fabric hand determines the tactile comfort perceived by humans and is incorporated with mechanical property (tensile, bending, shear, compression, and surface)

measurements by the Kawabata evaluation system. Although PCM microcapsules impart thermo-regulating properties to materials and thus improve the thermal comfort of clothing, they may affect other comfort-related properties and hand properties of the materials adversely, especially when the topical application of microcapsules results in drastic changes in the surface characteristics of materials. The extent of change in these properties depends on the loading amount of PCM microcapsules. Therefore, the performance properties of fabrics treated with PCM microcapsules need to be measured and considered before use in a garment (Shin, Yoo, & Son, 2005).

#### How does PCM work in textiles?

When the encapsulated PCM is heated to the melting point, it absorbs heat energy as it goes from a solid state to a liquid state. This phase change produces a temporary cooling effect in the clothing layers. The heat energy may come from the body or from the environment. Once the PCM completely melts, further storage of the heat stops. If the PCM garment is worn in an environment where the temperature is below the PCM's freezing point and the fabric temperature drops below the freezing point, the microencapsulated liquid PCM will change back to a solid state, releasing heat energy and generating a temporary warming effect. This heat exchange produces a buffering effect in clothing, minimizing changes in skin temperature and prolonging the thermal comfort of the wearer. It has also been claimed that using PCMs in outdoor clothing will decrease the required thickness and weight of the clothing. (Shim, Mccullough, & Jones, 2001)

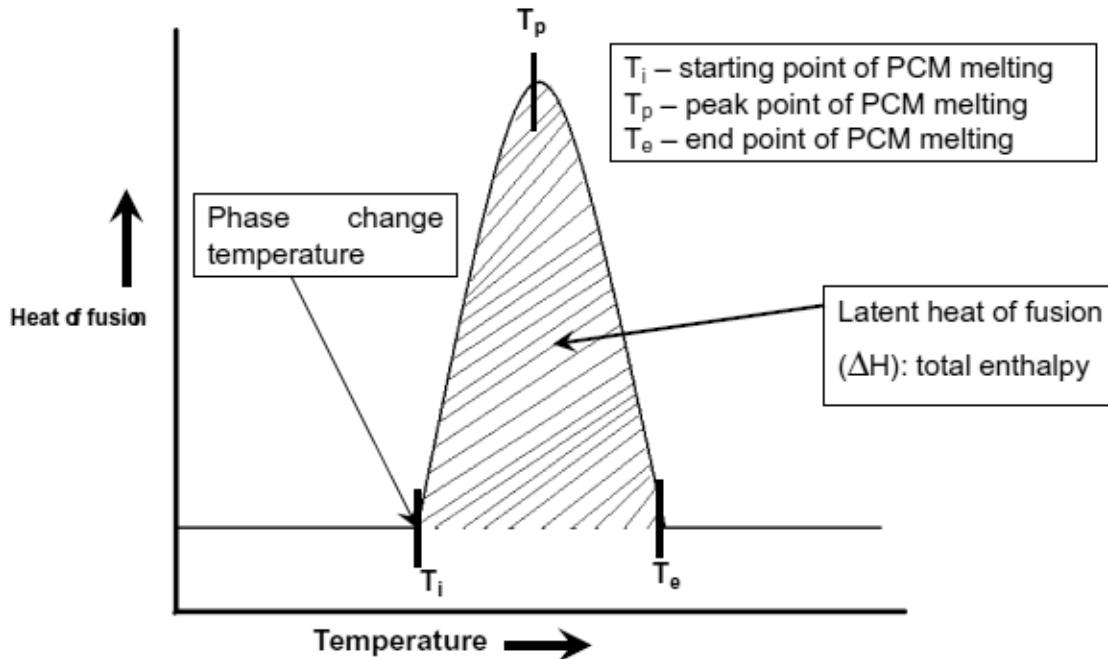


Fig. 2.2. Schematic DSC heating thermo-gram of PCM

When a PCM fabric is subjected to heating from the sun or a hot environment, it will absorb this transient heat as it changes phase from solid to liquid, and it will prevent the temperature of the fabric from rising by keeping it constant at the melting point of the PCM. Once the PCM has completely melted, its transient effect will cease and the temperature of the fabric will rise. In a similar manner, when a PCM fabric is subjected to a cold environment where the temperature is below its crystallization point, it will interrupt the cooling effect of the fabric structure by changing phase from liquid to solid and the temperature of the fabric will be kept constant at the crystallization point. Once all the PCM has crystallized, the fabric temperature will drop, and the PCM will have no effect on the fabric's thermal performance. Thus the thermal performance of a PCM depends on the phase change temperature, the amount of phase change material that is encapsulated, and the amount of energy it absorbs or releases.

during a phase change. (Ghali, Ghaddar, Harathani, & Jones, 2004) One major issue that needs to be addressed is that most PCMs have an unacceptably low thermal conductivity, and hence, heat transfer enhancement techniques are required for any latent heat thermal storage (LHTS) application. Various methods are proposed to enhance the heat transfer in a latent heat thermal store. Metallic fillers, metal matrix structures, finned tubes and aluminum shavings were used to improve paraffin's thermal conductivity (Farid, Khudhair, Razack, & Al-Hallaj, 2004).

Heat flows from warm body to the cooler environment, and there is a temperature gradient from the skin surface through the clothing layers to the environment. PCM microcapsules in the outermost clothing layer will not reach skin temperature, no matter how much body heat is produced during exercise. PCMS closest to the body will probably remain close to skin temperature and stay in the liquid state. PCMS in the outermost layers of clothing will probably get cold and solidify, thus producing some heat. However, in the outer layers of clothing, much of the heat released will flow to the cold environment, and the effect on body heat loss will be reduced accordingly. Once the PCM has changed from a liquid to a solid, the liberation of heat energy is over and will not continue. Therefore, the magnitude and duration of the heating and cooling effects of phase change materials in garments worn in different configurations on the body need to be documented (Shin, Yoo, & Son, 2005).

Water evaporation and movement in porous media are important phenomena, which can greatly affect the coupled heat and moisture transfer. Initial water content, surrounding temperature and batting thickness are also key factors influencing the heat flux through the clothing assemblies. Other parameters, such as the water vapor resistance of the outer and inner lining fabric, thermal conductivity of fiber, and porosity of porous batting, are found to have only a small effect (Fan, & Wen, 2002). A numerical simulation developed by Jintu Fan and Xizo-tin

Cheng reveals that inner fibrous battings with higher contents, finer fibers, greater fiber emissivity, higher air permeability, a lower disperse coefficient of surface free water, and a lower moisture absorption rate cause less condensation and moisture absorption, which is beneficial to thermal comfort during and after exercising in cold weather conditions (Fan, & Cheng, 2005).

Apart from introducing phase change materials in textile, scientists have also used other ways of creating a thermo-regulating effect in textile a few of them are listed below.

Active heating/cooling systems – Conductive materials can act as an electric resistance and can consequently be used as a heating element. On the other hand, cooling is a more complex process. Tiny cooling tubes are integrated in the jacket, and a liquid that is cooled by a central cooling element is circulated.

Adaptive insulation – DCTA (Defense Clothing & Textiles Agency), UK started research into the use of shape memory alloys for developing heat-protective clothing. In the experiment, springs made of a shape memory alloy (Nitinol) are used at room temperature. These springs are in a flat state at room temperature. At increasing temperatures the spring open up, thus making more air between the two layers, hence building the insulation.

Electric actuation – Electro-stimulation is the stimulation of muscles by electrical impulses. Electro-conductive textile structures can be used to take the electric impulses to any part of the body. Unfortunately, full remote control of this kind is yet to be adapted for use (Horrocks & Anand, 2000).

## Different types of PCMs

Phase change materials are theoretically able to change state at nearly constant temperature and therefore store large quantity of energy. Using the thermal energy storage (TES) of phase change material (PCM) that has a melting point from 15°C to 35°C is one of the most effective ideas for useful utilization of this kind of materials in textiles field. In addition to water, more than 500 natural and synthetic PCMs are known. These materials differ from one another in their phase change temperature ranges and their heat storage capacities. The required properties for a PCM to be used in a high efficiency cooling system having thermal energy system (TES) for specific application such as in textile fields are as follow:

- Melting point between 15°C and 35°C
- Large heat of fusion
- Little temperature difference between the melting point and the solidification point
- Harmless to the environment
- Low toxicity
- Non-flammable
- Stability for repetition of melting and solidification
- Large thermal conductivity, for effective heat transfer
- Ease of availability
- Low price

Based on the above properties, some of the PCM are known to be good for textile application; few of them are described briefly.

## Hydrated inorganic salt

Hydrated inorganic salt with “n” water molecules can be used in the manufacturing of heat storage and thermo-regulated textiles and clothing which usually has a heat absorbing and releasing temperature interval of about 20°C – 40°C. Physical and chemical properties of Glauber’s salts are very attractive for thermal storage: the salt has a convenient melting temperature (32.4°C) and melting latent heat of 254.00 kJ/kg which gives high energy at its melting point. Further, Mn(NO<sub>3</sub>)<sub>2</sub> . 6H<sub>2</sub>O is characterized by general availability, low toxicity and non-flammability.

## Linear long chain hydrocarbons

Hydrophobic linear hydrocarbon is a by-product of oil refining having a general formula of C<sub>n</sub>H<sub>2n+2</sub>. These are non-toxic and inexpensive, have extensive source of raw materials, and would be suitable for varied usage as they have a wide range of melting temperatures, depending on their carbon atoms. The melting and crystallization of hydrocarbon with n = 13–18 are in the range from 5.5°C to 61.4°C. By selecting the number of carbon atoms of hydrocarbon, the phase transition temperature could be tailored to specific applications.

## Polyethylene glycol (PEG)

Polyethylene glycol (PEG) is other important PCM for textile applications. Commercial paraffin waxes are cheap with moderate thermal storage densities (200kJ/kg or 150 MJ/m<sup>3</sup>) and a wide range of melting temperatures. The repeating unit of PEG is oxyethylene (–O–CH<sub>2</sub>–CH<sub>2</sub>–)<sub>n</sub>, with either end of chains comprising with hydroxyl group. The melting temperature of PEG is proportional to the molecular weight when its molecular weight is lower than 20,000. Differential scanning calorimetry can be used to evaluate PEG for latent heat thermal energy

storage. The formation of crystalline phase is influenced by the molecular weight of PEG. There is an increased tendency of higher-molecular-weight PEG towards the formation of crystalline phase owing to their lower segmental mobility and more convenient geometrical alignment. During the freezing cycle, an increase in the molecular weight of PEG causes an increase in the solidification temperature and heat of crystallization. It also influences the course of solidification by lowering the crystallization temperature ( $T_c$ ) (Scott, 2005).

Phase change materials are combination of different kinds of paraffin (octadecane, nonadecane, hexadecane, etc.) each with different melting and crystallization points. Changing the proportionate amount of each paraffin type can yield the desired physical properties. By careful selection of the phase change temperature, a PCM fabric can act as a transient thermal barrier by protecting the wearer of this fabric from the effect of cold and hot conditions (Ghali, Ghaddar, Harathani, & Jones, 2004).

This investigation deals with Polyethylene glycol of different molecular weights. The below table shows the melting behavior of different PEG (Scott, 2005)

Table 2.1

Molecular weight and melting point of polyethylene glycol (PEG)

Materials	Molecular weight	Melting point (°C) (approx. value)
PEG 1000	1000	35
PEG 1500	1500	50
PEG 3400	3400	59
PEG8000	8000	60
PEG10000	10,000	62
PEG20000	20,000	63

## Polyethylene glycol (PEG)

Polyethylene glycol (PEG) is a white, free-flowing powder or creamy white flakes and is used as a water soluble lubricant for rubber molds, textile fibers and metal forming operations. PEG has been considered a promising thermal energy storage material because of its relatively large heat of fusion, congruent melting behavior, non-corrosiveness and wide melting point range as a phase change material. In order to utilize PEG as a thermal energy storage material, it should not be degraded during the period of application. Thermal degradation of PEG produces low molecular weight products, which cause a lowering of the melting point and the heat of fusion. As thermal degradation proceeds, the amount of low molecular weight product becomes larger, and hence the performance of the thermal energy storage system declines (Han, Kim, & Kwon, 1997).

Osterhof studied the behavior of phase equilibrium in 10 aqueous sodium carbonate systems with different alkanethiols at temperature from 313.15 K to 363.15 K. They also studied PEG 200, PEG 400 and tri (ethylene glycol), which showed liquid – liquid equilibrium. The difference in miscibility of these increased with an increase in the molecular weight and decreased with an increase in the temperature (Taboada, Gruber, & Cisternas, 2004).

Chemical structure of PEG (Polyethylene glycol) FTIR spectra of PEG (Polu, & Kumar, 2011)



Fig. 2.3. Schematic figure of PEG chemical structure and FTIR peaks

## Microcapsulation

Microencapsulation is a technique by which solid, liquid, or gaseous active ingredients are packaged within a second material for the purpose of shielding the active ingredient from the surrounding environment. Thus the active ingredient is designated as the core material whereas the surrounding material forms the shell. This technique has been employed in a diverse range of fields from chemicals and pharmaceuticals to cosmetics and printing.

Microcapsules range in size from one micron (one thousandth of a mm) to few mm. Some microcapsules whose diameter is in the nanometer range are referred to as Nano capsules to emphasize their smaller size.

Microencapsulation of materials is resorted to ensure that the encapsulated material reaches the area of action without getting adversely affected by the environment through which it passes. Amongst the principal reasons for encapsulation are:

- Separation of incompatible components
- Conversion of liquids to free flowing solids
- Increased stability (protection of the encapsulated materials against oxidation or deactivation due to reaction in the environment)
- Masking of odor, taste, and activity of encapsulated materials
- Protection of the immediate environment
- Controlled release of active compounds (sustained or delayed release)
- Targeted release of encapsulated materials (Dubey, Shami, & Rao, 2009)

When PCMs are applied to textiles, they are surrounded by a protective shell to form a microcapsule of a few microns of diameter, to prevent diffusion of the core material during its liquid phase (Salaün, Bourbigot, & Rumeau, 2010).

Microencapsulation technology was utilized in the early 1980s by the US National Aeronautics and Space Administration (NASA) with the aim of managing the thermal barrier properties of garments, in particular for use in space suits. The microcapsules have walls less than 1 µm thick and are typically 20–40 µm in diameter, with a PCM loading of 80–85%. The small capsule size provides a relatively large surface area for heat transfer. Thus the rate at which the PCM reacts to an external temperature change is very rapid (Nelson, 2002).

The choice of the polymer for the membrane synthesis of the microcapsules is linked to the considered application and the required material processes. In the textile field, the polymers used must have good thermo mechanical properties to resist the thermal and mechanical requirements during the implementation processes and during the daily use by the wearer. The thermal properties of a microcapsule are influenced by three factors: its mean diameter, its expansion during the phase change process, and its shell's chemical structure (Salaün, Bourbigot, & Rumeau, 2010). Polyurethane/urea (PU) is a unique polymer with a wide range of physical and chemical properties such as abrasion resistance, water repellency, and leather appearance. These properties provided by PU coating to cotton or cotton-polyester blended fabrics are very attractive in many textile applications: transportation (e.g. car seats), apparel (e.g. waterproof breathable jackets), and furnishings (e.g. artificial leather upholstery; Giraud, 2005).

## Characterization of microcapsules

The characterization of the microcapsules can be performed using following methods.

### Optical microscopy (OM)

The optical microscopy technique provides images of microcapsules with a good resolution that allows a study of its morphology.

### Scanning electron microscopy (SEM)

SEM can be used to analyze the fixation and integrity of PCM microcapsules onto the coated textiles.

### Differential scanning calorimetry (DSC)

Measurements of phase change temperatures and energy storage capacities of different materials can be obtained using the DSC instrument. Different samples of each experiment should be analyzed at least three times, and the average value should be calculated. DSC analyses of coated textiles from random areas should be done.

### Infrared thermography

The infrared thermography allows measuring and observing surface temperatures with precision without having contact. Thermography utilizes the IR spectral band.

## Washing test

To test washing durability, the coated textiles should be treated on a short time program in a Gyrowash for 30 min at 40 °C, in accordance with ISO Standard 105-C06 (Sánchez, Sánchez-Fernandez, Romero, Rodríguez, & Sánchez-Silva, 2009).

The average microcapsule diameter is controlled by agitation rate;; the relationship between average diameter and agitation rate is linear in log-log scale, because of the dependence between droplet size and shear rate. Excess ammonium chloride or resorcinol, addition of smaller volumes of Dicyclopentadiene (DCPD), contaminated glassware, an unbalanced or unaligned mixer, and lower initial pH all dramatically increase the thickness of the outer, permeable layer. (Brown, Kessler, Sottos, & White, 2003) The microcapsules can be coated onto the fabric surface or can be embedded within the fiber based on the final application as illustrated in Figure 2.4 (a) Coated onto the fabric surface and (b) Microcapsules embedded within the fiber during fiber extrusion.

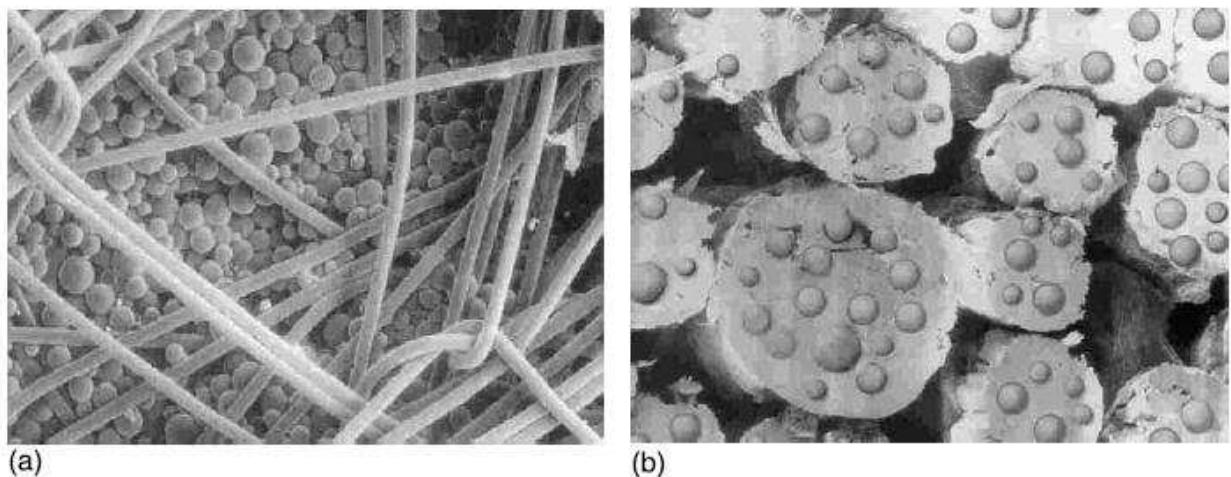


Fig. 2.4. SEM photographs of microcapsules

Other than encapsulating phase change material, microcapsules can also be used for applications like encapsulating fragrance for fragrance finishes, color changing technology, fire retardant fabric, counterfeiting, and liposomes (Nelson, 2002).

For the addition of microcapsules to textile material, the particle size and size uniformity are important factors. Colvin and Bryant used microencapsulated PCMs of 30–100 µm for textile fibers, composites, foams, and so forth. They also claimed that much larger particles of 1–3 mm could be placed within clothing layers to improve breathable thermal cooling under high humidity. The core/shell ratio, representing the PCM concentration and the shell, has to be as high as possible, and the shell has to be strong enough to secure capsule stability.

Microcapsules for textile materials should be stable against mechanical action such as abrasion, shear, and pressure. Stability test of the microcapsules can be evaluated by doing a repeated laundering test. For chemical stability evaluation, the microcapsules can be stirred in distilled water and alkaline solution at 20<sup>0</sup>C and 68<sup>0</sup>C at 380 rpm for 1 and 3 hrs. respectively. The study of any changes from these two tests can be found out by doing a morphology study under SEM.

From the study conducted my Younsook, Dong, and Kyunghee, it was seen that Polyurea microcapsules manufactured by interfacial polymerization were melted at curing temperatures higher than 80<sup>0</sup>C (Shin, Yoo, & Son, 2005).

### Fabric Coating

There are various coating processes such as knife over roll, knife over air, pad dry cure, gravure, dip coating, and transfer/cast coating. The study conducted by Kyeyoun Choi and Gilsoo Cho showed some interesting behavior with different microcapsule concentration over the

thermal properties. They used a coating mixture made by mixing microcapsules with an acrylic binder (Koplex TF-125) and urethane at a ratio of 9:1 in accordance with preliminary test. Coating mixture concentrations were 2:8 (20%), 3:7 (30%) and 4:6 (40%), the ratio of microcapsules to binder.

Thermal storage/release properties of microcapsules and specimens treated with microcapsules containing octadecane were analyzed by differential scanning calorimetry (DSC). The storage property was determined by measuring the melting temperature ( $T_m$ ) and the heat of fusion ( $H_m$ ) at 10-50 $^{\circ}$ C, and the release property by measuring crystallization temperature ( $T_c$ ) and heat of crystallization ( $H_c$ ) at 50 to -10 $^{\circ}$ C. The heating and cooling rates of the DSC run were both 10 $^{\circ}$ C/min. Heat of fusion, and heat of crystallization was obtained by calculating the peak area of the DSC curve.

To test wash fastness, the specimen were washed in an automatic washing machine with AATCC standard detergent in a normal washing cycle and tumble dried according to AATCC 135-1992. Mechanical properties, including tensile, bending, shear, compression, surface, thickness, air permeability, and weight were measured (Choi, Cho, Kim, & Cho, 2004).

## CHAPTER 3: RESEARCH AND METHODOLOGY

For a good research and scientific approach, proper selection of methodology, material, chemicals, and process control is essential. Various research techniques are tried to derive a final useful product, and documentation of each minute change in process is important for making the methodology consistent and reproducible. This chapter discusses the chemical contents, reaction process, various trial approaches, and their reasons for success and failure.

### Materials and Chemicals

Substrate – A 100% cotton mercerized and bleach fabric was used which had the below specifications.

EPI = 44 PPI = 38 Warp yarn count = 42 Weft yarn count = 42

### Chemicals

Sodium salt of dodecyl benzene sulfonic acid (SDS), Urea, Polyvinyl Alcohol (PVA), Formaldehyde, Triton x 100, Ammonium Chloride, Acetone, and 1,3-Benzenediol (Resorcinol) were obtained from Sigma Aldrich Chemicals Co. Ltd. Polyethylene glycol of various molecular weight such as PEG 1000  $\overline{M_w}$ , PEG 3400  $\overline{M_w}$ , and PEG 7500  $\overline{M_w}$  obtained from Polysciences, Inc. These chemicals were used without further purification after receipt from supplier.

### Experimental methods

During the research, many methods were adopted to get the final PEG microcapsules; a few of the methods were successful while others were not. The results of methods implemented are discussed below. Successful encapsulation method is described as follows.

Initially PEG was not encapsulated into the microcapsules that exhibited the absence of melting peak on the DSC graph. Aqueous media and a non-aqueous media are important for any encapsulation process. As PEG is soluble in water, it was difficult to form two different phases for the encapsulation process to take place. In this research, urea is an aqueous media which is soluble in water, and formaldehyde was used as a non-aqueous media. In order to prevent polyethylene glycol from dissolving in water and separating it out in the water for getting encapsulated, sodium carbonate was added and heated up to 40°C to get two layers (Taboada, Gruber, & Cisternas, 2004).

In order to form a good urea-formaldehyde resin, stoichiometric quantity of formaldehyde is added to the reaction.

According to the study done by Rochmad (Rochmadi, Prasetya, & Hasokowati, 2010), Citric Acid solution was used to reduce the pH of the solution in order to start the encapsulation process.

#### Encapsulation procedure for PEG 600

1. First, a mixture of polyethylene glycol (PEG600) and water is prepared in 250 ml glass beaker in which 25g of PEG is added to 100 ml of distilled water, followed by addition of 10g of sodium carbonate. The mixture is thoroughly stirred with the help of a magnetic stirrer at 600 rpm for 10 minutes. During this mixing, temperature is raised to 40°C using a hot plate. As a result, two separate layers of water and PEG are observed in this beaker.
2. A three-neck reactor is used for conducting the in-situ polymerization. The reactor is initially placed in an ice cold water bath to maintain the temperature between 15-20°C to avoid early polymerization reaction. A cold water condenser and a thermal probe were

connected to the reactor to condense the formaldehyde fumes and maintain the temperature during polymerization.

3. An aqueous prepolymer mixture containing 5% SDS, 4% PVA, 5% Triton X100, and 5% Resorcinol are added to the reactor. Resorcinol is added to achieve more cross-linking in urea-formaldehyde.
4. The PEG water mixture is then added to the reactor, and the mixture is stirred at 600 rpm for 15 minutes. While stirring the mixture, 30g of urea is added to the reactor. Two percent of Ammonium Chloride is added to the reaction. Thus, “oil-in-water system” is prepared, and colloidal dispersion containing PCMs is formed.
5. The stirring speed is then reduced to 300rpm and the pH is lowered to 3.5 – 4.0 by adding Citric acid.
6. Finally stoichiometric molar amount of 37% formaldehyde (15g) is added and the reaction is preceded for 50 min at 40°C.
7. After the reaction is completed, the solution is cooled down to 25°C; one layer of microcapsules floating over the top and some settled down at the bottom are observed. Both these layers are filtered out separately and then dried in the vacuum over for 12 hours to completely remove free formaldehyde from the microcapsules.

The dried microcapsules were then applied onto the fabric by soaking the fabric in the mixture of microcapsules and polyurethane. The coating mixture concentration was 20:80 (20%), the ratio of microcapsule to binder. The fabric is then passed through a padding mangle to remove excess solution and to get a uniform coating, which is followed by high temperature curing at 80°C inside the oven for two hours.

## Testing of PEG microcapsules and coated fabric

### Differential Scanning Calorimetry (DSC)

DSC graphs were used to study the thermal behavior of the microcapsules. A Q200 instrument from TA Instruments was used to do the DSC analysis. In the DSC instrument Tzero pans and Tzero lids were used for the samples. The sample weight used for the testing ranged from 8-12 milligram. The sample is sealed with the help of the supplied press in order to avoid any leakages into the DSC compartment.

After the sample is ready, it is placed into the DSC cell and Nitrogen is turned ON. The experiment is designed onto the computer in which parameters like temperature range, temperature change interval, weights of sample, type of test, and comments are entered. Once the test is completely done, the DSC graph is opened in the DSC analysis software where we can integrate the peaks to find the melting and crystallization peaks and the enthalpy given out or absorbed during these processes.

### Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity, or Raman scattering of a solid, liquid, or gas. FTIR study was important in my study to determine the presence of PEG in the microcapsules. The FTIR study was done on the instrument supplied by Bruker (Tensor 27) present in the lab.

The conical white disc is cleaned with acetone before starting the test to ensure there are no impurities left inside the chamber. Once this is done, a blank FTIR spectrum is taken; this helps in calibrating the machine and gives us a good tool for comparison.

The PEG microcapsules were pressed and crushed with the help of a spatula to take out the PEG which can be tested before putting the sample into the chamber. The FTIR spectrum is taken and the peaks are marked out with the help of a peak-finding tool to get the wavelength of all the peaks shown on the spectrograph.

### Scanning Electron Microscopy (SEM)

SEM was used to study the morphology of the developed microcapsules. A S-3400 N model from Hitachi was used to capture the photographs by placing the sample inside the chamber at a magnification of approx. 1.2 k at 12 kV and 20 probes current.

### Textile testing for physical and chemical properties

Testing physical properties of the textile material is very important to see the effect of the microcapsule coating onto the fabric properties. This ensures that other fabric properties are not affected due to the application of new coating onto the fabric surface, or the extent of the effect can be easily known.

Fabrics were tested to tensile, tear, stiffness, air permeability, and thickness. Other tests like comfort testing and thickness testing were also done.

### Tensile testing

This test calculates the breaking force which is the maximum force applied to a material carried to rupture. The MTS tensile tester was used to determine the tensile force; this instrument works on CRE (constant rate of extension) principle. In CRE testing machines the rate of extension of the specimen length is uniform with time. ASTM D 5035 – 95 test method was used for the testing. Ten specimens were cut in the warp and weft direction. The specimens of size 1”

x 8" were cut and clamped between the two jaws, which are set 6" apart. Peak load and break elongation were noted, and standard deviation of the results was found out.

### Tearing Strength

This test method covers the measurement of the tearing strength of textile fabrics by the tongue procedure using a recording constant rate of extension (CRE) type tensile testing machine. The same MTS tester used for testing tensile force was used to test the tearing strength. The test was carried out by following the ASTM D 2261 – 96 test method. Five specimens in warp and weft direction were tested for calculating the tear strength.

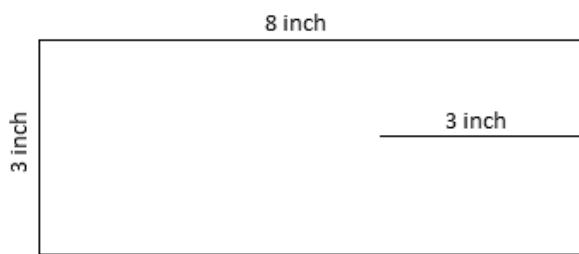


Fig. 3.1. Specimen dimension for tear strength testing

The specimen size of 8-inch length and 3-inch width with a 3-inch slit as shown in the above figure was prepared. The specimen was secured in the clamp jaws with the slit edge of each tongue centered in such a manner that the originally adjacent cut edges of the tongue formed a straight line joining the centers of the clamp, and the two tongues presented opposite faces of the fabric to the operator.

The tearing graph was recorded by the machine. The top five peaks were marked, and its corresponding load value is noted. An average value was then taken out to get the tearing strength of that particular sample.

## Air permeability

Air permeability of the coated fabric and the uncoated cotton sample was tested using the Faizer instrument model No. 1081. The appropriate nozzle was screwed into the chamber below the table. The door was then latched closed firmly. The size of the nozzle used in testing depends on the porosity of the material under test. The nozzle should be small enough that the red oil of the vertical manometer reaches at least 3" line. (The machine is not accurate below the 3" line)

Fabric to be tested was clamped on the 2 ¾ inch diameter test opening on the top of the table. The transformer switch was then placed in the “on” position and its knob was slowly rotated to increase the speed of the blower. It was made sure to proceed carefully not to run the oil over the top of the manometer. The speed of the motor was adjusted until the inclined manometer reads 0.5" of water. The position of the red oil in the vertical manometer was observed and noted after it was stabilized. The corresponding air flow in terms of cubic feet per minute was taken from the column of the used nozzle size.

The result for the odd number readings were found out with the help of interpolation by using the below formula.

$$y_2 = \frac{(x_2 - x_1)(y_3 - y_1)}{(x_3 - x_1)} + y_1$$

Ten readings from different areas of each sample were noted to get the correct estimation of the air permeability of the fabric.

### **Thickness measurement**

Thickness of the fabric was measured using Elektro Physik precision standard 526  $\mu\text{m} \pm 1\%$  on the Minitest 600B coating thickness gauge as per ASTM D1777-96 method. This coating thickness gauge is battery powered and equipped with 1 m probe cable. It works on the magnetic induction principle and should be used for measuring non-magnetic coatings such as aluminum, chrome, copper, paint, and rubber on iron or steel substrates. Average and standard deviations of coating thickness are reported.

### **Stiffness Testing**

This test method covers a procedure to measure the resistance to bending using the Taber type tester (ASTM D 5342 – 97). Five test specimens of 1.5inch x 2.75 inch are cut in warp and weft direction. Each sample is then clamped and bent 15° from its center line to right and left hand side of the testing instrument. The resultant bending moment was recorded from the instrument scale, and resistance to bending was calculated by using the below formula.

Stiffness values in millinewton.meters = Taber unit x 0.098066

### **Comfort Testing**

Thermal and Evaporative Resistance of clothing materials was measured using a MTNW incorporation made Sweating Hot Plate ( Serial # 223-21) inside the TPS Lunaire Climatic Chamber ( Model # CEO 910 -4) according to ASTM F 1868 -02.

Thermal resistance of the fabric was measured by first measuring the bare plate thermal resistance using the test plate software. For the bare plate test, humidity and temperature of the chamber was maintained at 65% and 21°C. The humidity sensor and wind sensor should be connected correctly to the controller. The wind sensor should be adjusted at a height of 7 mm using a block of height 7 mm on the plenum and according to fabric thickness; plenum can be

raised or lowered in order to maintain that gap. The Rcbp ASTM F 1868-02 test was started from the test program. After the test reached the steady state, and temperature and heat flux were in tolerance for 30 minutes; then the test was saved and exited. The average of the thermal values was used to calculate the thermal resistance of fabric. Rct (ASTM F 1868-02) test measures the resistance of bare plate plus the resistance of fabric in the similar way as Rcbp was measured by placing the fabric sample (10" x10") on the test plate and taping it on all the edges.

Bare plate moisture resistance was calculated according to ASTM F1868-2 as Reb<sub>p</sub>. resource tank as filled with deionized water and then the water tube connecting to sight glass was connected to the test plate, and water was pushed using a pump by placing a thumb on the sight glass. Water should be pumped such that the test plate is completely wet and water is coming from all the holes on the test plate. Extra water was removed using a sponge. Cellophane film was used because when it is wet, it resembles the skin and moisture can pass through this, but not the water. Cellophane was completely wet on one side and then placed on the test plate. Cellophane was trimmed from the side and then scotch blue painter's tape was used to hold it on all four sides. The height of the wind sensor on the top of the test plate was adjusted using a black metal block. Then Reb<sub>p</sub> test was run on the software and continued till the temperature and heat flux remained in steady state and in tolerance for 30 minutes. After this, Moisture resistance of the fabric plus the bare plate (Ret) was evaluated by placing the fabric on cellophane.

Finally, moisture resistance of fabric was calculated by subtracting the Reb<sub>p</sub> from Ret. Similarly, thermal resistance of the fabric was calculated by subtracting Rcbp from Rct.

## CHAPTER 4: RESULTS AND DISCUSSION

This research was carried out to develop a new in-situ polymerization technique to encapsulate Polyethylene Glycol (PEG) of different molecular weights. This technique was developed so that ultimately a thermo regulating fabric can be developed to increase the human comfort. Second, I consider this method suitable for laboratory scale work as well as industrial production while considering some important issues like time-saving. This chapter discusses the test results and the procedures adopted for successful encapsulation of PEG.

Diverse chemical encapsulation techniques are described in literature. Of special interest for this work is the in-situ polymerization in an oil-in-water emulsion with encapsulating water-immiscible liquids by the reaction of urea with formaldehyde at acidic pH.

### Synthesis of urea-formaldehyde polymer

The synthesis of urea-formaldehyde polymer takes place in two stages. In the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino group of urea. This reaction is actually a series of reactions that lead to the formation of monomethyolurea, dimethyolurea, and trimethyolurea.

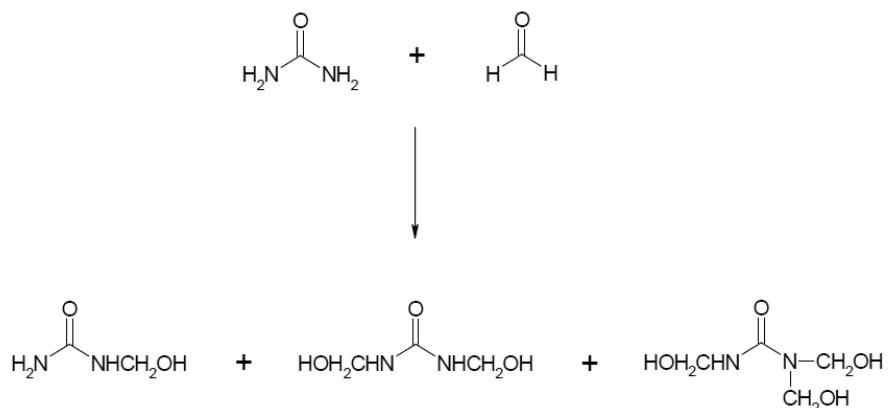


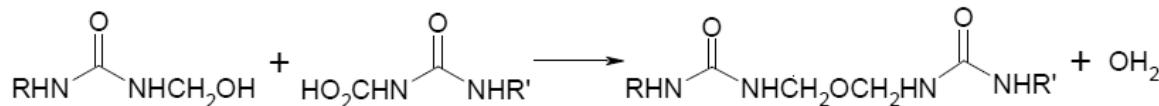
Fig. 4.1. Formation of mono-, di- and trimethyolurea by the addition of formaldehyde to urea

The second stage of the urea-formaldehyde resin synthesis consists of the condensation of the methylolurea to low molecular weight polymers. The increase in the molecular weight under acidic conditions to produce higher molecular weight oligomers and polymers is a combination of the following reactions: Reaction of methylol and amino groups of the reacting molecules leading to methylene bridges between amino nitrogen (Fig. 4.2a); reaction of two methylol groups which builds methylene ether linkages (Fig. 4.2b); splitting out of formaldehyde from methylene ether linkages, results in methylene linkages and (Fig. 4.2c); reaction of methylol groups in which water and formaldehyde is separated out and methylene linkages are obtained (Fig. 4.2d).

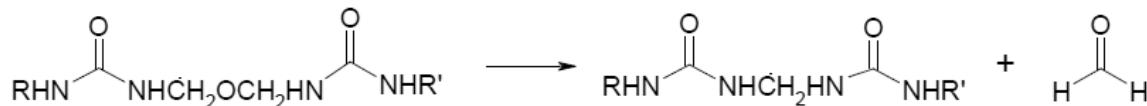
(a)



(b)



(c)



(d)

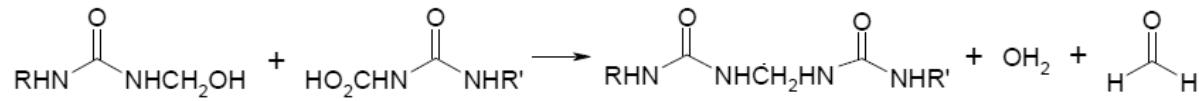


Fig.4.2. Second stage reactions of the urea formaldehyde polymerization, forming higher molecular weight oligomers and polymers

### FTIR Analysis of encapsulated PEG microcapsules

Infrared spectroscopy was done to confirm the formation of urea-formaldehyde microcapsules. The main reason behind doing the FTIR analysis was to confirm the presence of PEG 600. For this, the microcapsules were first crushed using a spatula so that the encapsulated PEG can be taken out for FTIR analysis showing the characteristic peaks.

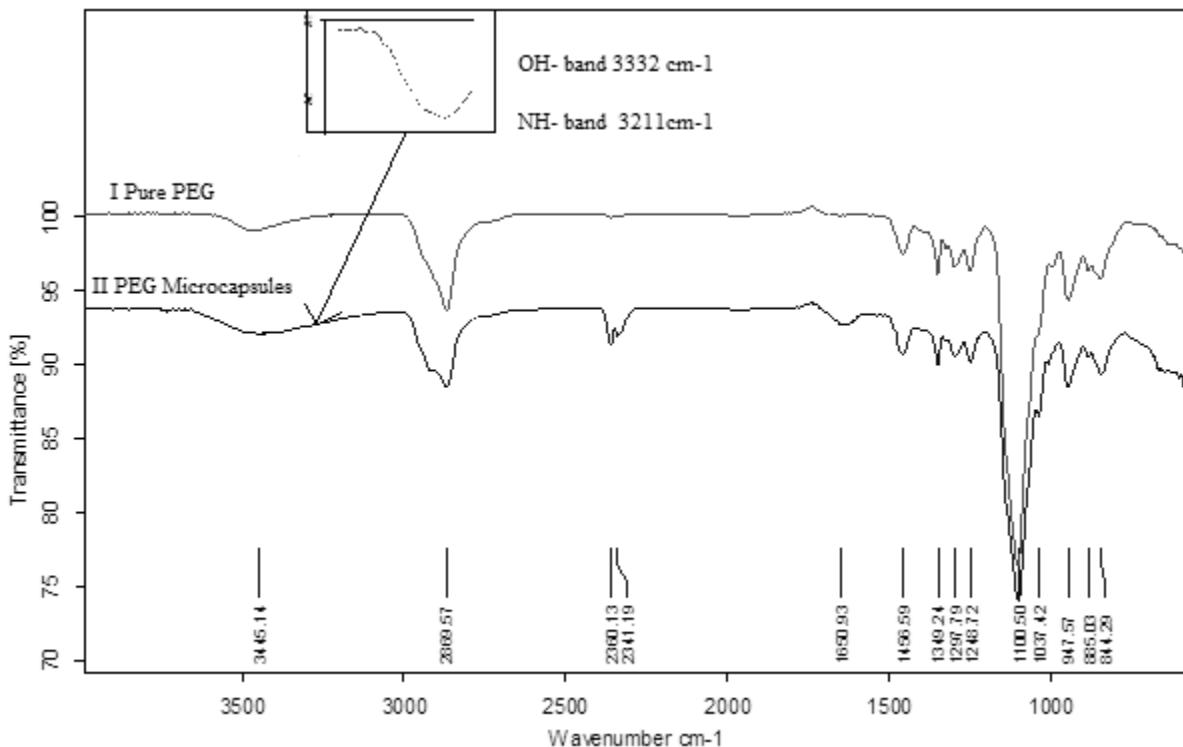


Fig. 4.3. FTIR spectrogram of pure PEG (I) and encapsulated PEG microcapsules (II)

The resulting FTIR spectra of both samples, the pure PEG (I) and PEG encapsulated microcapsules (II), show the expected peaks at  $3211\text{ cm}^{-1}$ ,  $1650\text{ cm}^{-1}$ , and around  $1400\text{ cm}^{-1}$ , which are the characteristic absorption peaks of  $-\text{NH}$  and  $-\text{C=O}$  stretching vibrations as well as  $-\text{CH}$  bending vibration, respectively.

The spectrum of the urea-formaldehyde PEG microcapsules shows a strong absorption band at  $3332\text{ cm}^{-1}$ . This band is broad and typical of hydrogen bonded N-H and OH. One strong absorption is observed at  $1650\text{cm}^{-1}$  which has been assigned to carbonyl C=O stretching vibration indicating the presence of tertiary amide. Appearance of OH peak relatively broad at  $3360 -3390\text{ cm}^{-1}$  is due to hydrogen bonding. The information obtained from the IR spectra of the urea-formaldehyde PEG microcapsule is consistent with structure given in the Figure 4.2d. These three primary peaks indicate the formation of the urea-formaldehyde wall material.

As expected the resulting spectra of the PEG encapsulated microcapsules exhibited strong  $\text{CH}_2$  stretching vibrations near  $2800\text{ cm}^{-1}$  that attributes the absorption peaks of PEG. As appears from the peak magnitude of both pure PEG and encapsulated PEG, microcapsules a good amount of PEG was encapsulated inside the microcapsules. However, it is necessary to reconfirm the encapsulation by another analytical method like DSC.

## DSC Analysis of encapsulated PEG microcapsules

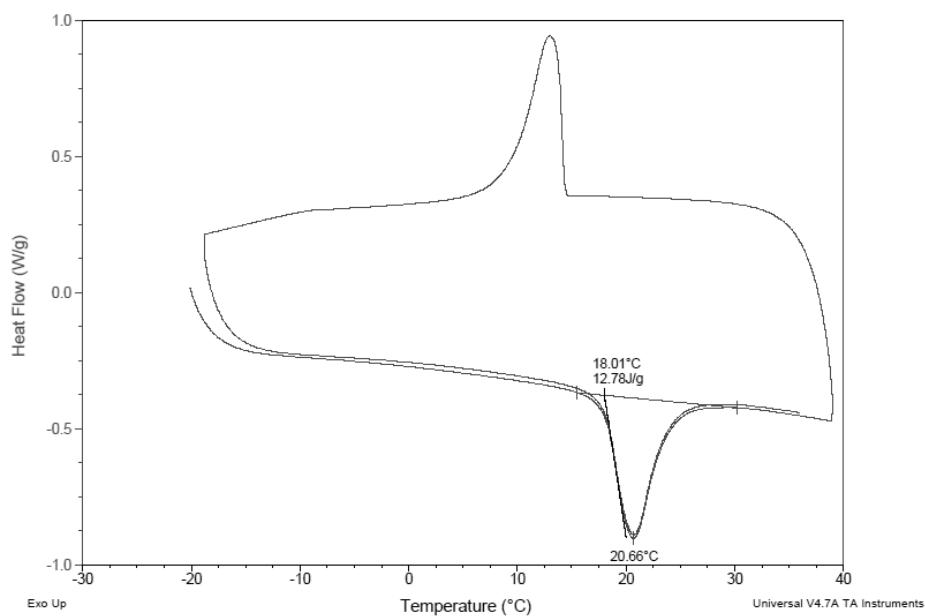


Fig. 4.4. Thermo graph of microcapsules from DSC analysis

The heat cool heat analysis was done of the microcapsules to examine the thermal behavior of PEG. The samples were cooled down at  $-20^{\circ}\text{C}$  and then heated up to  $40^{\circ}\text{C}$  at a constant rate of  $10^{\circ}\text{C}/\text{min}$ . The phase change temperature  $T_m$  of the microcapsules was found to be around  $21^{\circ}\text{C}$  and was similar to that of the pure PEG 600 as determined by the analysis of neat PEG. The heat storage capacity of the microcapsule was  $12.78\text{J/g}$ . When the PCM 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 PCM microcapsules are cooled down below the freezing point of PCM material, the material will change back to solid state from the liquid state, releasing heat and thus developing a temporary warming effect. Near  $12^{\circ}\text{C}$  the recrystallization of the PCM material can be seen 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. After a repetitive heating of the sample, the melting point obtained from of the DSC thermo gram remained the same, indicating the stability of the material at higher and lower temperature variations.

#### Scanning Electron Microscopy (SEM) study of encapsulated PEG microcapsules

The SEM study was done to study the morphology of the microcapsules. The pictures were taken at various magnifications to get clear pictures for better morphology study.

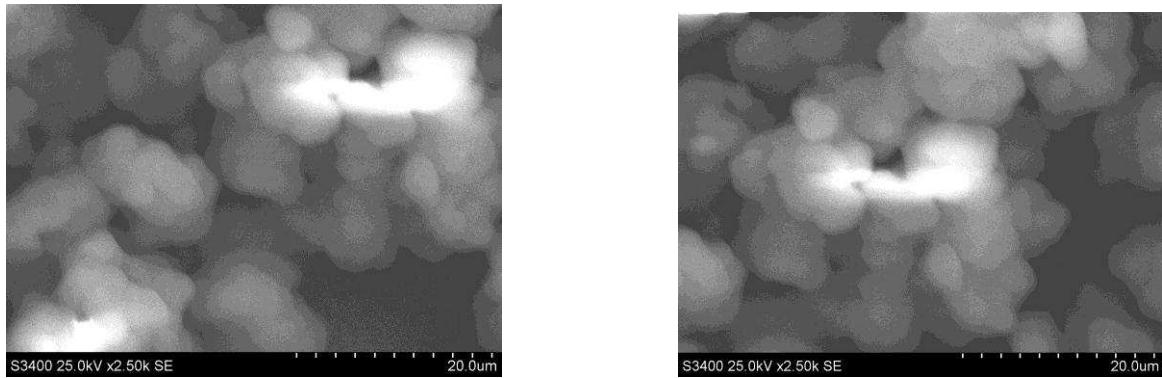


Fig. 4.5. SEM pictures showing the uniform and circular diameter

The average diameter of the developed microcapsules was calculated to be around 30  $\mu\text{m}$ . This indicates that the microcapsules are tiny and easy to coat onto the fabric surface.

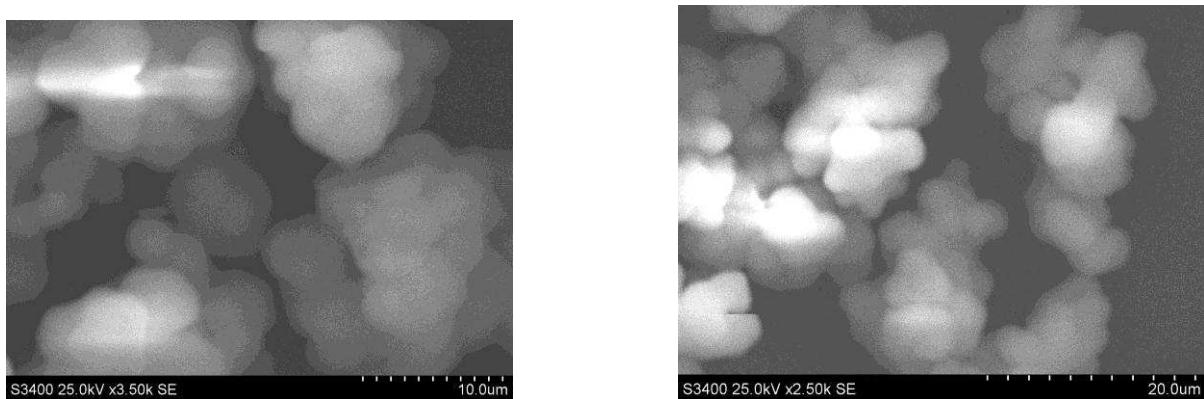


Fig. 4.6. SEM pictures showing the round, spherical, and smooth morphology of the microcapsules

Particles which had an irregular shape found at the bottom of the reactor were identified as nano particles which didn't hold any PEG inside them. The floating microcapsules in the reactor were found to have a smooth surface as shown in Figure 10 and contained PEG inside them.

#### Testing of fabric's physical properties

##### Tensile testing

The tensile testing of the coated fabric was done on an MTS tester by using the ASTM D 5035. Test specimens were tested in both warp and weft directions. The maximum peak load and elongation at break was recorded. (Appendix A.1)

Mean and standard deviation of tensile strength values are reported in Table 4.1

Table 4.1

Coated and Uncoated fabric tensile strength values

	N	Minimum	Maximum	Mean	Std. Deviation
Uncoated warp	11	34.47	42.60	38.9183	2.57733
Uncoated weft	11	17.10	22.97	20.5913	1.74701
Coated warp	11	26.91	39.63	32.5459	4.54003
Coated weft	11	21.81	31.11	27.6293	2.89888
Valid N (list wise)	11				

From the results shown in Table 4.1, 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 polyurethane coating.

### Tear Strength

Most of the textile fabrics are subjected to tear when in use, so it's very important to confirm the tear properties of the fabric after the treatment. The method used for calculating the tear strength was ASTM D 2261. The tear strengths for uncoated and coated fabric were recorded in both warp and weft direction. (Appendix A.2)

The mean and standard deviation of tear strength values are reported in Table 4.2

Table 4.2

Coated and uncoated fabric tear strength values

	N	Minimum	Maximum	Mean	Std. Deviation
Tear coated Weft	6	1.75	1.85	1.8000	.04290
Tear coated Warp	6	1.94	2.42	2.2660	.17591
Tear uncoated weft	6	1.85	2.20	2.0400	.11679
Tear uncoated warp	6	2.20	2.70	2.5200	.17205
Valid N (list wise)	6				

Table 4.2 shows a decrease in tear strength in weft direction. This may be because of increase in stiffness of the fabric due to the application of coating.

### Air permeability of fabric

Air permeability of the fabric is one of the prime contributors to the comfort properties of the fabric. This was calculated on the Frazier air permeability testing machine. An 8mm and

6mm nozzle were used for uncoated and coated fabric, respectively. The readings shown onto the horizontal barometer were then interpolated with the figures given in the air flow rate chart. The interpolated values of flow of air in cubic cm, per Square cm of sample per Second at 30" Mercury were noted. (Appendix A.3)

Table 4.3

Coated and uncoated fabric air permeability values

	N	Minimum	Maximum	Mean	Std. Deviation
Coated	10	45.45	73.90	60.8190	9.04964
Uncoated	10	78.72	97.94	88.0650	5.27200
Valid N (list wise)	10				

From the calculated air permeability results, it is observed that there is a significant difference in the air permeability of the coated fabric. It is concluded that the air permeability of the fabric was significantly reduced due to the presence of polyurethane coating. Therefore, thickness of the coating needs to be optimized.

#### Stiffness testing

Taber type test instrument was used to determine the stiffness of the uncoated and coated fabric sample. The ASTM method used was D 5342, and the stiffness of the sample was calculated in warp and weft direction. The measurements of the bending force were noted (Appendix A.4) and then multiplied by 0.098066 to convert the bending force to milli-newton.

The calculated bending force is given below

Warp stiffness (Coated) –  $0.9 \times 0.098066 = 0.08825$  milli-newton

Weft stiffness (Coated) –  $1.2 \times 0.098066 = 0.11767$  milli-newton

Warp stiffness (uncoated) –  $0.6 \times 0.098066 = 0.05883$  milli-newton

Weft stiffness (uncoated) –  $0.8 \times 0.098066 = 0.07845$  milli-newton

Table 4.4

Coated and uncoated fabric stiffness values

	N	Minimum	Maximum	Mean	Std. Deviation
Coated warp	5	.50	1.00	.9000	.22361
Coated weft	5	.50	1.50	1.2000	.44721
Uncoated warp	5	.00	1.50	.6000	.54772
Uncoated weft	5	.50	1.00	.8000	.27386
Valid N (list wise)	5				

The results derived from Table 4.4 do not show a significant change in stiffness of the fabric after being coated with the microcapsules. Thus the garments made from the coated fabric will show similar stiffness properties of the uncoated fabric.

#### Thickness Measurement

The thickness measurement was done using ASTM D1777-96 method, and the thickness values of both the sample were noted at ten different places to get uniform results. (Appendix A.5)

Table 4.5

Coated and uncoated fabric thickness values

	N	Minimum	Maximum	Mean	Std. Deviation
coated	10	785.00	905.00	824.0000	38.49964
uncoated	10	745.00	765.00	755.0000	7.45356
Valid N (list wise)	10				

From the results we can conclude that the thickness of the coated fabric is much higher than that of the uncoated fabric sample. Even if the diameter of the microcapsule was measured to be 30µm, the thickness of the fabric is much higher than the original fabric thickness, this given an opportunity for further research on the process of application onto the fabric surface.

#### Comfort testing

The thermal and evaporative resistance values are important to test for a thermo regulating fabric. This test can give us an idea of how the fabric will behave on the human skin. The test was conducted according to the ASTM F-1868. The thermal resistance and evaporative resistance value were noted for analysis. (Appendix A.6 and A.7)

Table 4.6

Coated and uncoated fabric comfort values

Uncoated Fabric Sample		Coated Fabric Sample	
Thermal resistance Rct-Rcbp	Evaporative resistance Ret-Rebp	Thermal resistance Rct-Rcbp	Evaporative resistance Ret-Rebp
0.034241	2.741033	0.041023	5.377325

From the test results mentioned in Table 4.6 we can observe a 20% increase in thermal resistance of the fabric sample coated with microcapsules. This proves that microcapsules are playing a good role in resisting the heat transfer and regulating the body temperature. This test was conducted at an elevated temperature by sending steam through the hot plate. This heat is observed by the PCM microcapsules and therefore, heat was not sensed by the instrument above the fabric.

## CHAPTER 5: CONCLUSION

This study was done to develop an in-situ polymerization technique to encapsulate various molecular weight of Polyethylene glycol (PEG). The PEGs used in the study were PEG  $\bar{M}_w$ 600, PEG  $\bar{M}_w$ 1000, and PEG  $\bar{M}_w$ 3400. The thought behind using different molecular weight PEG was because of their different melting temperature and different enthalpy required for melting which can be used to match the requirements of the specific end use.

But the method developed was only successful in encapsulating PEG  $\bar{M}_w$ 600 and was not capable of encapsulating the other two higher molecular weights of PEG. A different approach in chemistry for encapsulation by using different chemical instead of sodium carbonate to form two immiscible layers of PEG and water can prove beneficiary to develop an effective method.

People are giving higher preference to comfort by using 100% cotton or other such fibers which are comfortable to the body. Thus application of PCMs in daily wear in addition to the industrial use, will increase in the future, bringing potential research and business.

Objective 1: Develop an in-situ polymerization technique to encapsulate various molecular weights of PEG.

Conclusion 1: An effective in-situ polymerization technique was developed which requires less time (50 min) for encapsulation of PEG  $\bar{M}_w$ 600. The technique failed to encapsulate the higher molecular weight PEG.

Objective 2: Application of the formed microcapsules on the fabric surface by coating.

Conclusion 2: Successful coating technique was developed by using polyurethane, which was then coated onto the surface using a padding mangle.

Objective 3: DSC analysis of the encapsulated phase change material.

Conclusion 3: The DSC analysis showed the melting peak of PEG 600 which confirmed its presence inside the microcapsules. Other tests like FTIR and comfort test were also done to support the DSC analysis and to prove that PEG 600 can be a good phase change material for textile application.

Objective 4: Testing the physical properties of the posted treatment sample.

Conclusion 4: Various physical property evaluations were done to confirm the performance properties of the fabric. There was an increase in warp tensile strength due to the coating, but the weft tearing strength was recorded to be reduced because of the higher stiffness due to the polyurethane coating; this increase in stiffness was also reconfirmed by doing the stiffness measurement. It was concluded from the test observations that the air permeability of the fabric was significantly reduced due to the presence of polyurethane coating, which can be observed by the thickness measurements. Therefore, thickness of the coating needs to be optimized. The comfort test results confirmed the thermal regulation capabilities of the PCM microcapsules. A 20% increase in thermal resistance of the fabric sample coated with microcapsules was confirmed.

I have shown that the microencapsulation method presented in this study, based on in situ polymerization technique, was quite successful in producing microcapsules with an enhanced thermal capacity in relation to the PCM content. Microcapsules performed their function effectively under both heating and cooling conditions, and endothermic and exothermic phase transitions took place within the intervals coinciding with those of PCMs. SEM photos illustrate many distinct spheres of perfectly smooth surface morphology.

Considering the process conditions employed in the manufacture of polyurea-formaldehyde shells encapsulating paraffin waxes, that is, low stirring rates, low heating requirement, short polymerization duration, ordinary atmosphere and atmospheric pressure, and so on. I have concluded that this procedure, completely differing from some of the microencapsulation techniques, is adequate and easy to apply for the industrial-scale production, and does not bring difficulties, that is, high energy consumption and long duration.

The thermal properties of fabrics including microencapsulated PCM can be designed to be dynamic and actively responsive for some special end-use fields.

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## Appendix A: Fabric Test Result

### A.1 Tensile Strength Results

#### Grab Test

Specimen – 1” x 8” with specimen length between the jaws equal to 6”.

Sr. No.	Uncoated Sample (lbf)		Coated Sample (lbf)	
	Warp	Weft	Warp	Weft
1	34.466	22.170	30.608	21.811
2	42.075	19.588	26.911	27.307
3	37.027	18.190	39.632	22.855
4	37.568	20.051	38.217	29.826
5	37.529	21.384	35.111	30.386
6	41.797	21.738	26.922	29.179
7	40.847	22.974	33.416	31.113
8	38.118	21.345	28.327	28.084
9	42.600	21.370	37.077	27.907
10	37.156	17.103	29.238	27.825
Avg.	38.9183	20.5913	32.5459	27.6293

### A.2 Tear Strength Results

Tear strength Results				
Sr. No.	weft tear coated	warp tear coated	weft tear uncoated	warp tear uncoated
1	1.85	2.42	2.2	2.5
2	1.76	2.34	2	2.6
3	1.79	2.4	2.04	2.2
4	1.85	2.23	2.11	2.7
5	1.75	1.94	1.85	2.6
Avg.	1.8	2.266	2.04	2.52

### A.3 Air Permeability Test Results

Air permeability test results Rate of air in cubic CM, per Square CM of sample per second at 30" mercury				
Sr. No	Coated fabric		Uncoated fabric	
	Scale reading	Interpolated value	Scale reading	Interpolated value
1	5.2	55.88	4.8	97.94
2	8	69.6	3.8	86.7
3	5.5	57.35	3.6	84.82
4	3.5	45.45	3.8	86.7
5	9	73.9	4.2	91.76
6	9	73.9	4	89.7
7	5.2	55.88	3.1	78.72
8	5.6	57.88	4.3	92.79
9	5.5	57.35	3.6	84.82
10	6.2	61	3.8	86.7
Avg.		60.819		88.065

### A.4 Stiffness Test Results

Stiffness test results				
Sr. No.	Coated Sample		Uncoated Sample	
	Warp	weft	Warp	weft
1	1	0.5	0.5	0.5
2	1	1.5	1.5	1
3	0.5	1.5	0.5	1
4	1	1	0.5	1
5	1	1.5	0	0.5
Avg.	0.9	1.2	0.6	0.8

## A.5 Thickness Test Results

Fabric Thickness Measurement		
Sr. No.	Coated ( $\mu\text{m}$ )	Uncoated ( $\mu\text{m}$ )
1	840	745
2	815	750
3	865	760
4	830	750
5	795	765
6	785	755
7	905	745
8	825	760
9	795	765
10	785	755
Avg.	824	755

## A.6 Thermal Resistance Properties

Dry Thermal resistance Results

Test method ASTM F1868

Room Temperature = 25°C

Relative Humidity = 65%

Hot Plate Temperature = 35°C

Specimen Dimension = 10 x 10 inch

Sr. No.	Sample Detail	Dry Bare Plate (Rcbp)	Dry Thermal Resistance (Rct)	Sample Dry Thermal Resistance (Rct-Rcbp)
1	Un-coated Fabric	0.053211	0.087452	0.034241
2	Coated Fabric	0.052258	0.093281	0.041023

## A.7 Evaporative Resistance Properties

Test method ASTM F1868

Room Temperature = 25°C

Relative Humidity = 65%

Hot Plate Temperature = 35°C

Specimen Dimension = 10 x 10 inch

Sr. No.	Sample Detail	Wet Bare Plate (Rebp)	Evaporative Resistance (Ret)	Sample Evaporative Resistance (Ret-Rebp)
1	Un-coated Fabric	4.55455	7.295583	2.741033
2	Coated Fabric	4.845385	10.22271	5.377325

# Phase change materials for smart textiles – An overview

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## Abstract

Phase change materials (PCM) take advantage of latent heat that can be stored or released from a material over a narrow temperature range. PCM possesses the ability to change their state with a certain temperature range. These materials absorb energy during the heating process as phase change takes place and release energy to the environment in the phase change range during a reverse cooling process. Insulation effect reached by the PCM depends on temperature and time. Recently, the incorporation of PCM in textiles by coating or encapsulation to make thermo-regulated smart textiles has grown interest to the researcher. Therefore, an attempt has been taken to review the working principle of PCM and their applications for smart temperature regulated textiles. Different types of phase change materials are introduced. This is followed by an account of incorporation of PCM in the textile structure are summarized. Concept of thermal comfort, clothing for cold environment, phase change materials and clothing comfort are discussed in this review paper. Some recent applications of PCM incorporated textiles are stated. Finally, the market of PCM in textiles field and some challenges are mentioned in this review paper.

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**Keywords:** Phase change materials; Clothing comfort; Microencapsulation; Smart temperature adaptable fabrics

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## 1. Introduction

Fundamental principles of science are now increasingly employed for the manufacturing of innovative textile products. One such principle is ‘Phase Change’, the process of going from one physical state to another i.e. from a solid to a liquid and vice versa. Fibre and textile which have automatic acclimatising properties have recently attracting more and more attention. This effect could be achieved by using phase change material (PCM) [1]. The technology for incorporating PCM microcapsules [2] into textile structure to improve their thermal performance was developed in the early 1980s under NASA research programme. The original intent was to use these fabrics in the astronauts’ space suits to provide improved thermal protection against the extreme temperature fluctuations in outer space. From

the original application of astronauts suits, the PCM incorporated textiles taking the market place of consumer apparel products.

Thermal energy storage (TES) is the temporary storage of high or low temperature energy for later use. It bridges the time gap between energy requirements and energy use [3]. 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 [4,5].

Phase change materials possess the ability to change their state with a certain temperature range. These materials absorb energy during the heating process as phase change takes place, otherwise this energy can be transferred to the environment in the phase change range during a reverse cooling process [6]. The insulation effect reached by the PCM is dependent on temperature and time; it takes

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place only during the phase change (in the temperature range of the phase change) and terminates when the phase change in all of the PCMs would complete. Since, this type of thermal insulation is temporary; therefore, it can be referred to as dynamic thermal insulation. Numerous engineering application has made the topic of melting of phase-change material in enclosures one of the most active fields in heat transfer research today [7].

Textiles containing phase change materials react immediately with changes in environmental temperatures, and the temperatures in different areas of the body. When a rise in temperature occurs, the PCM microcapsules react by absorbing heat and storing this energy in the liquefied phase change materials. When the temperature falls again, the microcapsules release this stored heat energy and the phase change materials solidify again [8]. The thermal insulation capabilities of cold protective clothing materials may be significantly improved by the incorporation of Micro-PCM, these capsules containing small amounts of PCM. Manufacturer can now use phase change material to provide thermal comfort in wide variety of garments. The use of phase change materials, which absorb energy during heating and release energy during cooling, improve the thermal insulation capacity which differs significantly from the insulation properties of any other material [9]. Currently this property of PCMs is widely exploited in various types of garments. PCM microcapsules could be directly incorporated into fibres, and foams, or typically applied to fabrics as a coating. In this article an account of PCM, working principle with textile structure and the application PCM incorporated textiles are reported.

## 2. Phase change processes

Latent heat storage is one of the most efficient way of storing thermal energy. Unlike the sensible heat storage method, the latent heat storage method provides much higher storage density, with a smaller temperature difference between storing and releasing heat [10]. Every material absorbs heat during a heating process while its temperature is rising constantly. The heat stored in the material is released into the environment through a reverse cooling process. During the cooling process, the material temperature decreases continuously. Comparing the heat absorption during the melting process of a phase change material (PCM) with those in normal materials, much higher amount of heat is absorbed if a PCM melts. A par-

affin-PCM, for an example, absorbs approximately 200 kJ/kg of heat if it undergoes a melting process [10]. High amount of heat absorbed by the paraffin in the melting process is released into the surrounding area in a cooling process starts at the PCM's crystallization temperature. After comparing the heat storage capacities of textiles and PCM, it is obvious that by applying paraffin-PCM to textiles their heat storage capacities can substantially enhanced [6].

During the complete melting process, the temperature of the PCM as well as its surrounding area remains nearly constant. The same is true for the crystallisation process; during the entire crystallisation process the temperature of the PCM does not change significantly either. Phase change process of PCM from solid to liquid and vice versa is schematically shown in Fig. 1. The large heat transfer during the melting process as well as the crystallization process without significant temperature change makes PCM interesting as a source of heat storage material in practical applications. When temperature increases, the PCM microcapsules absorbed heat and storing this energy in the liquefied phase change materials. When the temperature falls, the PCM microcapsules release this stored heat energy and consequently PCM solidify [10].

The phase diagram of the binary system of tetradecane-hexadecane (Fig. 2) has been thoroughly discussed by He et al. [11,12]. Because the pure tetradecane ( $C_{14}H_{30}$ ) and hexadecane ( $C_{16}H_{34}$ ) solid have similar structure (triclinic crystals), the binary system contains all conditions for formation a solid solution [12]. Phase diagrams (equilibrium diagrams) depict the concentration–temperature–pressure relationships of a chemical system at equilibrium and are used to visualise how these relations change with temperature and chemical composition. The upper curve ( $T - x_{i(l)}$ ) in Fig. 2 is the liquidus or freezing point curve. The lower curve ( $T - x_{i(s)}$ ) is the solidus or melting point curve. Any system represented by a point above the liquidus is completely molten, and any point below the solidus represents a completely solidified mass. A point within the area enclosed by the liquidus and solidus curve indicates an equilibrium mixture of liquid and solid solution. These two curves approach and touch at point  $M$ , which is the minimum-melting point. The phase transition occurring on the cooling of a given mixture has been described by He et al. [11,12]. The phase transition temperature range for each homogenous liquid can be obtained directly from the phase diagram. The storage density of mixtures,

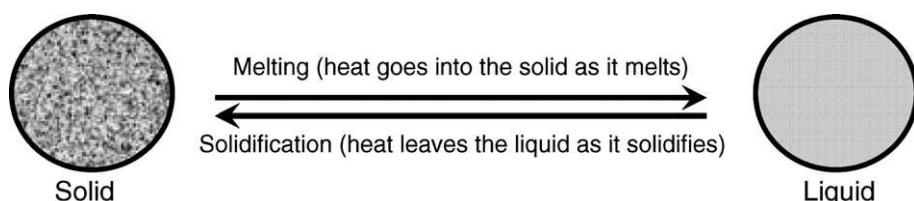


Fig. 1. Schematic representation of phase change process.

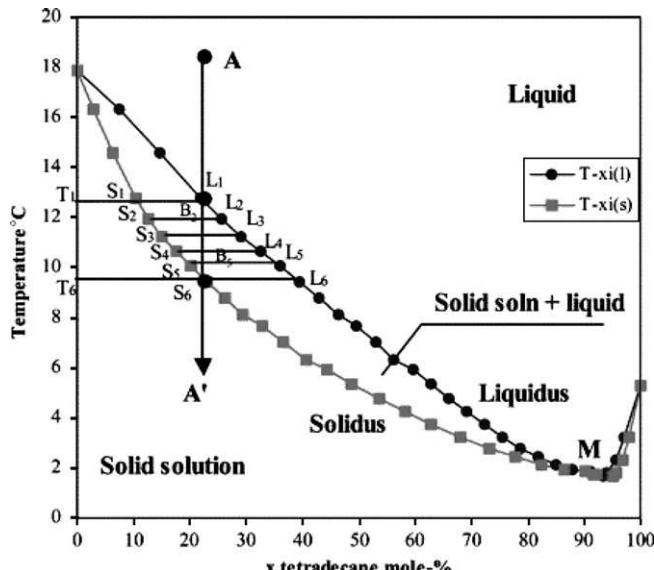


Fig. 2. The liquid-solid phase diagram of binary mixtures system of  $C_{14}H_{30}$  and  $C_{16}H_{34}$  (reproduced with permission from [11]).

corresponding to a certain temperature range within the phase transition temperature range, can be obtained by using the “lever principle” from the phase diagram. The phase transition temperature range of mixtures is the function of the composition of mixtures, and the storage density in any temperature range is the function of composition and temperature change.

### 3. Working principle of phase change materials (PCMs)

Thermal energy storage is an essential technique for thermal energy utilization [13]. For thermal energy storage there are four alternatives viz. sensible heat utilization, latent heat utilization, utilization of reversible chemical heat, and utilization of heat of dilution. Material has four state viz. solid, liquid, gas and plasma. When a material

converts from one state to another, this process is called phase change. There are four kinds of phase change, such as (a) solid to liquid (b) liquid to gas (c) solid to gas and (d) solid to solid. Heat is absorbed or release during the phase change process. This absorbed or released heat content is called latent heat. PCM which can convert from solid to liquid or from liquid to solid state is the most frequently used latent heat storage material, and suitable for the manufacturing of heat-storage and thermo-regulated textiles and clothing.

Modes of heat transfer are strongly depends [14] on the phase of the substances involve in the heat transfer processes. For substances that are solid, conduction is the predominate mode of heat transfer. For liquids, convection heat transfer predominates, and for vapors convection and radiation are the primary mode of heat transfer. For textile applications, we will only consider the phase change from solid to liquid and vice versa. Therefore, the principle of solid to liquid phase change and vice versa would be discussed. When the melting temperature of a PCM is reached during heating process, the phase change from the solid to the liquid occurs. Typical differential scanning calorimetry (DSC) heating thermogram for PCM melting is schematically shown in Fig. 3. During this phase change, the PCM absorbs large quantities of latent heat from the surrounding area. PCM may repeatedly converted between solid and liquid phases to utilize their latent heat of fusion to absorb, store and release heat or cold during such phase conversions.

Phase change materials as such are not new [15,16]. They already exist in various forms in nature. The most common example of a PCM is water at 0 °C, which crystallizes as it changes from liquid to a solid (ice) [6,16]. A phase change also occurs when water is heated to a temperature of 100 °C at which point it becomes steam. In order to compare the amount of heat absorbed by a PCM during the actual phase change with the amount of heat absorbed in an ordinary heating process; water can be used for

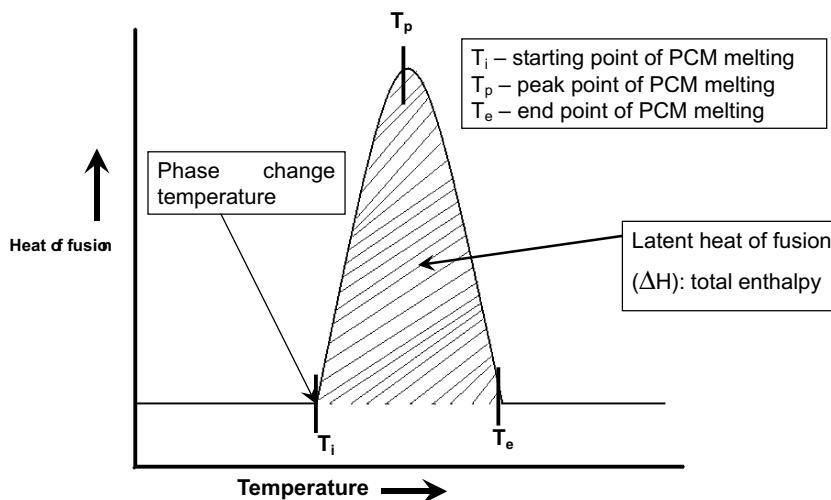


Fig. 3. Schematic of DSC heating thermogram of PCM.

comparisons. When ice melts into water it absorbs approximately a latent heat of 335 kJ/kg. When water is further heated, a sensible heat of only 4 kJ/kg is absorbed while the temperature rises by one degree celcius.

#### 4. Different types of PCMs

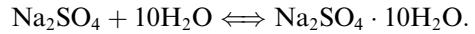
Phase change materials are able theoretically to change state at nearly constant temperature and therefore to store large quantity of energy [17]. Using the thermal energy storage (TES) of phase change material (PCM) which has a melting point from 15 to 35 °C is one of the most effective ideas for effective utilization of this kind of materials in textiles field. In addition to water, more than 500 natural and synthetic PCMs are known [18]. These materials differ from one another in their phase change temperature ranges and their heat storage capacities. The required properties for a PCM for a high efficiency cooling system with thermal energy system (TES) for specific application [19] such as in textile fields are as follow:

- (i) melting point between 15 and 35 °C;
- (ii) large heat of fusion;
- (iii) little temperature difference between the melting point and the solidification point;
- (iv) harmless to the environment;
- (v) low toxicity;
- (vi) non-flammable;
- (vii) stability for repetition of melting and solidification;
- (viii) large thermal conductivity, for effective heat transfer;
- (ix) ease of availability;
- (x) low price.

A wide spectrum of phase change material is available with different heat storage capacity and phase change temperature. A simple and classical example of phase change materials is the paraffin wax leads ranging from 15 to 40 µm in size, which can be microencapsulated and then either integrated into fiber or used as a coating. Some of the PCMs are describes in the following paragraphs:

##### 4.1. Hydrated inorganic salt

Hydrated inorganic salt with '*n*' water molecules, can be used in the manufacturing of heat storage and thermo-regulated textiles and clothing which usually, has a heat-absorbing and -releasing temperature interval of about 20–40 °C. Physical and chemical properties of Glauber's salts are very attractive for thermal storage: the salt has a convenient melting temperature (32.4 °C) and melting latent heat of 254.00 kJ/kg which gives high energy at its melting point [20]. In the thermal energy system (TES), using sodium sulfate water solution as the PCM, heat produced or absorbed by the following chemical reaction between the decahydrate crystal and the water solution [21]:



The mode of a crystallizing process, which occurs by cooling the TES capsule continuously, differs significantly depending on the initial temperatures being higher or lower than 32 °C. When the capsule is cooled down from a temperature higher than 32 °C to a temperature lower than 32 °C, a process of crystal nucleation in a supersaturated solution appears. When the initial temperature is lower than 32 °C, the heat removal process is explained by a phenomenon of crystal growth where crystal nuclei or small crystals already existing in the solution increase in size. Hydrated salts are attractive materials for use in thermal energy storage due to their high volumetric storage density (~350 MJ/m<sup>3</sup>), relatively high thermal conductivity (~0.5 W/m °C) and moderate costs compared to paraffin waxes. Glauber salt ( $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ), which contains 44%  $\text{Na}_2\text{SO}_4$  and 56%  $\text{H}_2\text{O}$  by weight has been studied [22,23].

Manganese(II) nitrate hexahydrate ( $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) has 125.9 kJ/kg heat of fusion. Its density is nearly  $1.8 \times 10^3 \text{ kg/m}^3$ , and this means a latent heat per unit volume of  $226.6 \times 10^3 \text{ kJ/m}^3$ . It contains 68% that of water, and the melting point is 25.8 °C. The temperature difference between the melting and the solidification point was found to be quite large. Further, the  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is characterized by general availability, low toxicity and non-flammability [19].

##### 4.2. Linear long chain hydrocarbons

Hydrophobic linear hydrocarbon is by product of oil refining having general formula of  $\text{C}_n\text{H}_{2n+2}$ . These are non-toxic, inexpensive, and have extensive source of raw materials, would be suitable for varied usage as they have wide range of melting temperature depending on their carbon atoms (Fig. 4). The melting and crystallization of hydrocarbon with  $n = 13\text{--}18$  are in the range from –5.5 to 61.4 °C [24]. By selecting the number of carbon atom of hydrocarbon, the phase transition temperature could be tailored for specific applications. From Fig. 4, we can see that *n*-Eicosane have melting temperature is about human body temperature. They might be the most important PCMs in the manufacture of heat storage and thermo-regulated textiles and clothing. The performance of thermoregulation would depends on the heat adsorption and heat emission of the hydrocarbons. The heat adsorption and heat emission of some linear hydrocarbons are listed in Table 1.

##### 4.3. Polyethylene glycol (PEG)

Polyethylene glycol (PEG) is another important PCMs for textile applications. Commercial paraffin waxes are cheap with moderate thermal storage densities (~200 kJ/kg or 150 MJ/m<sup>3</sup>) and a wide range of melting temperatures [10]. The repeating unit of PEG is oxyethylene ( $-\text{O}-\text{CH}_2-\text{CH}_2-$ )<sub>*n*</sub>, with either end of chains comprising with

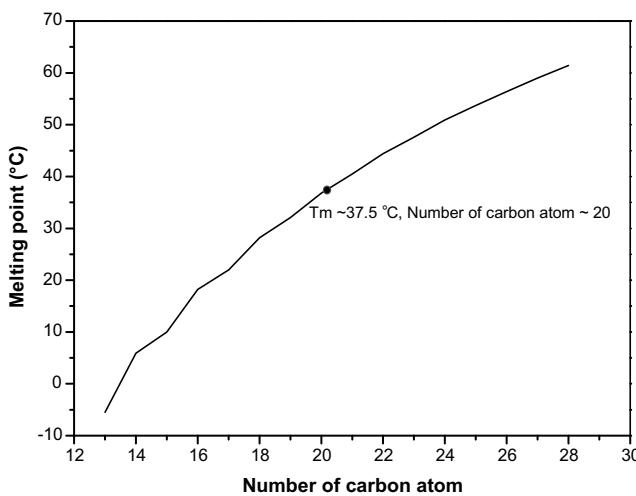


Fig. 4. Paraffin hydrocarbon and their melting temperature [24].

hydroxyl group. The melting temperature of PEG is proportional to the molecular weight; when it's molecular weight is lower than 20,000. Differential scanning calorimetry can be used to evaluate PEG for latent heat thermal energy storage. The formation of crystalline phase would influences by the molecular weight of PEG; there is an increased tendency of higher-molecular-weight PEGs towards the formation of crystalline phase owing to their lower segmental mobility and more convenient geometrical alignment. During the freezing cycle, an increase in the molecular weight of PEG causes an increase in the solidification temperature and heat of crystallization. It influences also the course of solidification by lowering the crystallization temperature ( $T_c$ ). An additional effect observed in the case of the blend's freezing is associated with larger supercooling, probably due to morphological constraints and entanglements in interlamellar regions. The possible advantage of using PEG blends to replace pure components is connected with the possibility of changing the temperature range and heat associated with melting/freezing [27]. The melting point temperature of PEG would depend on the molecular weight of polymer (Table 2).

#### 4.4. Others

Feldman and Shapiro [32] have analyzed the thermal properties of fatty acids (capric, lauric, palmitic and stearic acids) and their binary mixtures. The results have shown

Table 2  
Molecular weight and melting point of polyethylene glycol (PEG)

Materials	Molecular weight	Melting point (°C) (approx. value)	Ref.
PEG 1000	1000	35	[28]
PEG 1500	1500	50	[29,30]
PEG 3400	3400	59	[29,30]
PEG8000	8000	60	[31]
PEG10000	10,000	62	[29,30]
PEG20000	20,000	63	[29,30]

that they are attractive candidates for latent heat thermal energy storage in space heating applications. The melting range of the fatty acids was found to vary from 30 to 65 °C, while their latent heat of transition was observed to vary from 153 to 182 kJ/kg. These properties are of prime importance in the design of a latent heat thermal energy storage system. In their natural form, fats and vegetable oils melt at temperatures useful for thermal energy storage. Incremental improvement of their heat release characteristics could pave the way for commercial applications as phase change materials (PCM). These chemicals could provide a biomaterial alternative to a technology dominated by paraffin and salt products [33].

Thermal phase change properties of some other PCM are as follows: butyl stearate, melting point (m.p.) = 19 °C, f.p. = 21 °C, heat of fusion ( $\Delta H_m$ ) = 120 kJ/kg, vinyl stearate, m.p. = 27 °C, f.p. = 29 °C,  $\Delta H_m$  = 122 kJ/kg, isopropyl stearate, m.p. = 14 °C, f.p. = 18 °C,  $\Delta H_m$  = 142 kJ/kg seem promising [34].

#### 5. Thermal conductivity enhancer for PCM

One of the most commonly used PCMs in storing thermal energy is the paraffin. The advantage of PCM storage compared to sensible heat-storage systems, is its potential to store large amounts of heat with only a small temperature swing. However, PCMs have some disadvantages, such as the low heat-conductivity of the material [35]. The thermal conductivities of most PCMs are too low to provide a required heat exchange rate between the PCM and substrate. Therefore, thermal conductivity enhancer would be useful to efficiently use the thermal energy stored in the PCM [36]. The thermal conductivities of PCM could be enhanced by using metal filler, carbon nanofiber/fiber fillers etc [36–39]. Carbon fibers have a strong resistance to corrosion and chemical attack, which make

Table 1  
Latent heat of adsorption and emission [24–26]

Hydrocarbons	No of C atoms	Ref. [24]	Latent heat of adsorption ( $\Delta H$ ) in J/g	Latent heat of emission ( $-\Delta H$ ) in J/g	Crystallization temperature ( $T_c$ , °C)	Ref.
n-Hexadecane	16		235.2	236.6	12.2	[25]
n-Heptadecane	17		176.4	182.6	16.5	[25]
n-Octadecane	18		244.8	246.4	22.0	[25]
n-Nonadecane	19		177.6	182.6	26.4	[25]
n-Eicosane	20		242	230	30.4	[26]

them compatible with most PCMs. The thermal conductivities of carbon nano-fibers are considerably high and their densities are less than  $2260 \text{ kg/m}^3$ , which is lower than those of metals that are usually used as additives [37]. Therefore, carbon nanofiber (CNF)/fiber could be used as efficient thermal conductivity enhancer for PCM useful for textile applications. The CNF could be introduced into the PCM by using shear mixing and melting techniques. It is common knowledge in heat transfer that when lateral surface area increases, the heat transfer rate increases. The thermal properties of the modified PCM could be enhanced significantly by dispersing CNFs into it [37]. As a result of this enhancement, the cooling rate during the solidification process of the new nanocomposite increased significantly by increasing the mass ratio of the CNFs.

The effectiveness of thermal conductivity enhancers (TCEs) in improving the overall thermal conductance of phase change materials (PCMs) has been studied by Nayak et al. [40]. For the case of PCM with porous TCE matrix, it was observed that inserting aluminum matrix into Eicosane can offer an order-of-magnitude increase in thermal conductivity and melting rate. Melt convection has a considerable effect on the evolution of the solid–liquid interface. However, the effect of convection becomes insignificant beyond a certain volume fraction of TCE. For the case of PCM with TCE fins, too, convection in the melt plays a significant role in temperature uniformity. The performance of the heat sink improves if the TCE material is distributed in the form of thinner fins. It is also found that rod-type fins perform better than plate-type ones, as they are able to maintain better uniformity of temperature within the PCM leading to less chip temperature [40].

The numerical approach makes it possible to calculate the processes that occur inside the solid PCM (conduction), liquid PCM (convection), and air (convection) simultaneously, and to account for the phase-change, moving boundary due to the variation of the PCM volume, and solid phase motion in the melt [41]. The paraffin (*n*-dodecane)/expanded graphite (EG) composite PCMs can be easily prepared by impregnation of liquid paraffin into the porous structure of EG. The paraffin/EG composite PCM with mass fraction of 10% EG would be accepted as form-stable composite PCM as it allowed no leakage of melted paraffin from the pores of EG when subjected to a solid–liquid phase change process. In particular, the use of form-stable composite PCM can reduce the weight of the latent heat thermal energy storage (LHTES) system due to its low density besides its direct usability in energy storage systems without a requirement of an extra storage container. Increasing the mass fraction of EG from 2% to 10% gradually increased the thermal conductivity of paraffin/EG composite PCM. A very high correlation ( $r = 0.9986$ ) occurred between thermal conductivity and mass fraction of EG, indicating a strong association between the two attributes [5].

## 6. Fire hazard treatment of paraffin

One of the problems we are still facing is the burning behavior of the PCM layer, as the microcapsules are mostly made of paraffin. Flame propagation can be stopped by adding a flame retardant treatment to the coating but there was still a hole formation at the place where the flame was applied. Possible solutions of this problem are the improvement of the flame retardant treatment or the use of the PCM in a sandwich construction between two fabrics [42]. Cai et al. prepared stable phase change material (PCM)-high density polyethylene (HDPE)/paraffin hybrid with different flame-retardant systems by using twin-screw extruder technique. The weight of char residues of flame-retardant form-stable PCMs are markedly higher than that of the form-stable PCM. Although, its latent heat is given by differential scanning calorimetry (DSC) method, which showed the latent heat of PCM had not distinct change with the addition of flame retardant. In other words, the property of thermal energy storage has not been affected by the addition of flame retardants [43]. A kind of form stable phase change material (PCM) based on high density polyethylene (HDPE), paraffin, organophilic montmorillonite (OMT) and intumescence flame retardant (IFR) hybrids is reported by Cai et al. [44]. The synergy between OMT and IFR leads to the decrease of the heat release rate (HRR), contributing to improvement of the flammability performance. The DSC analyses indicate the latent heat of the form stable PCM has no distinct change with the loading of the IFR and OMT. A kind of shape stabilized phase change nanocomposites materials (PCNM) based on high density polyethylene (HDPE)/ethylene–vinyl acetate (EVA) alloy, organophilic montmorillonite (OMT), paraffin and intumescence flame retardant (IFR) are prepared using twin-screw extruder technique [45]. The paraffin acts as a phase change material and disperses in the three-dimensional network structure. The TGA analysis results indicate that the flame retardant shape stabilized PCNM produce a larger amount of char residue at  $800^\circ\text{C}$  than that of shape stabilized PCNM, although the onset of weight loss of the flame retardant shape stabilized PCNM occur at a lower temperature. The formed multicellular char residue contributes to the improvement of thermal stability performance.

## 7. Concept of thermal comfort

The heat exchange with the environment plays a key role in the thermal state of the human body [46]. Thermal comfort is defined as that condition of mind which expresses satisfaction with the thermal environment. Dissatisfaction may be caused by warm or cool discomfort for the body in general, as expressed by the predicted mean vote (PMV) and predicted percentage of dissatisfied (PPD) indices [47]. However, thermal dissatisfaction may also be caused by an unwanted heating or cooling of one particular part of the body (local discomfort). The PMV and PPD

indices express warm and cool discomfort for the body as a whole. Due to individual differences, it is impossible to specify a thermal environment that will satisfy everybody. A percentage of the occupants can always be expected to be dissatisfied. Nevertheless, it may be possible to specify environments predicted to be experienced as acceptable by a certain percentage of the occupants. In the new standard, comfort requirements are specified predicted to be acceptable for at least 80% of the occupants [48]. The indoor air quality is quite mediocre in many air-conditioned or mechanically ventilated buildings, even though existing standards may be met. The aim should be to provide indoor air that is perceived as fresh, pleasant and stimulating, with no negative effects on health, and thermal environment perceived as comfortable by almost all occupants [49]. The impact of enthalpy on acceptability or on perceived air quality expressed in percentage dissatisfied or decipol is strong. Humans obviously like a sensation of cooling of the respiratory tract each time air is inhaled. This causes a sensation of freshness which is felt pleasant. If proper cooling does not occur, the air may feel stale, stuffy and unacceptable. A high enthalpy means a low cooling power of the inhaled air and, therefore, an insufficient convective and evaporative cooling of the wet mucous membranes in the respiratory tract, and in particular the nose. Heat loss through respiration is only around 10% of the total heat loss from the body, and humidity and temperature of the inhaled air has, therefore, only a small impact on the thermal sensation for the human body as a whole [49]. Therefore, clothing would play prominent role as far comfort to the wearer is concerned. The transport of dry heat through a fabric is a complex process involving conduction, convection and radiation. Transport of sensible heat flow from the skin of a dressed subject to a cooler environment is even more complicated. Warm air can be pressed through the fabric layers of the clothing and through small and large openings of the clothing to the surrounding environment, and cold air can be sucked into the clothing. Within the clothing, mixing of air layers of different temperatures can be caused by compression and extension of air-filled cavities. An additional influence of wind may further enhance the complexity of heat exchange [50]. The dry heat loss,  $H_{dry}$ , from the skin can be calculated from the heat balance equation as:

$$H_{dry} = M - W - C_{res} - E_{res} - E - S.$$

where  $M$  is the metabolic rate,  $W$  is the external work,  $C_{res}$  is the convective respiratory heat loss,  $E_{res}$  is the evaporative respiratory heat loss,  $E$  is the evaporatory heat loss from the skin and  $S$  is the change in body heat content. With, all values are expressed in  $\text{W m}^{-2}$ .

During activity, body movements lead to circulation of air trapped in the clothing and thus to increased convective heat transfer and lower  $I_{cl}$  (intrinsic clothing insulation) values. Also, surface air insulation  $I_a$  is reduced by body movements. This reduction is caused by changes in the heat transfer coefficient,  $h$ , because the convective heat transfer

coefficient,  $h$ , is increased [50]. Thermal neutrality for a person is defined as a condition in which he prefers neither a higher nor a lower ambient temperature level. Thermal neutrality is a necessary condition for a person to attain thermal comfort but this condition is not always sufficient. A further requirement is that no local warm or cool discomfort is experienced on any part of the body; asymmetric radiation may create such local discomfort [51].

Personalized ventilation can improve occupants' thermal comfort, perceived air quality and decrease the intensity of sick building syndromes (SBS) symptoms compared to mixing ventilation. Occupants will use the provided individual control of airflow rate and positioning of the air terminal device to obtain preferred microenvironment in rooms where the air temperature is within the range recommended by indoor climate standards. Under mixing ventilation the thermal sensation approached the slightly warm level for both whole body and local ratings. In the second condition, personalized ventilation systems (PVS) provided local cooling that resulted in a whole body thermal sensation close to neutral. The cooling was even more visible for the head region, for which the thermal sensation was almost neutral. The difference between local thermal sensation with mixing ventilation and PVS was significant throughout the whole experiment ( $P < 0.01$ ). The thermal sensation felt with PVS was in general perceived as more acceptable than the sensation with mixing ventilation ( $P < 0.05$ ) [52]. The improvement in perceived air quality with PVS depends on the room air temperature and the temperature difference between room and personalized air. The greatest improvement was observed when the temperature of the personalized air was lower than the room air [52].

## 8. Clothing for cold environments

For predicting or evaluating the indoor thermal environment, clothing is an important factor. In most cases clothing is selected individually by the occupants. In some cases, however, the type of clothing is prescribed by the workplace (e.g., clean room, uniforms and dress codes). The indoor air temperature may affect also the clothing adjustment, i.e. the attitude of people to change their clothes in a workplace [53]. Because of the limitations of their physiological defenses against cold, humans are generally obliged to supplement those defenses by clothing and shelter, which reduce the thermo-regulatory challenge to an endurable and usually comfortable level. Reduced discomfort from cold is accompanied by increased discomfort from heat. A nude person in the cold experiences sustained vasoconstriction, shivering, and sometimes a fall in deep body temperature. Fully clothed people in the Antarctic occasionally suffer these responses (mainly during light work, or when their clothing is wet or cannot be adjusted), but their most characteristic thermo-regulatory experience is alternating vasoconstriction and vasodilatation [54]. The bioheat human model is capable of predicting accurately nude human transient physiological responses such

as the body's skin, tympanic, and core temperatures, sweat rates, and the dry and latent heat losses from each body segment. The nude body model is integrated to an existing clothing model based on heat and mass diffusion through the clothing layers and takes into consideration the moisture adsorption by the fibers [55]. In cold environments, appropriate assessment of working time limits is important to avoid unacceptable body cooling during work. At low temperatures both general body cooling and local cooling can limit the working time because of discomfort, deteriorated extremity performance and, in more extreme cases, due to cold injury. Duration limited exposure (DLE) index, which provides a method to determine acceptable time limits when, in a cold environment, clothing insulation is not sufficient to protect wearer from body cooling [56]. DLE is defined as the maximal exposure time with the existent clothing insulation and can be determined at two levels strain, a lower level starting from thermo-neutral conditions (DLE<sub>neu</sub>) and a higher level starting from the body slightly cooled (DLE<sub>min</sub>). Heat balance, defined as preservation of the initial core temperature was maintained at all ambient temperatures at the time limits predicted by DLE, although at the expense of different levels of peripheral cooling. The energy expenditure (EE) of the subjects was higher with the lighter clothing than with the heavier clothing during the mild cold exposure and male subjects were satisfied thermally with the environment. Since the EE was affected by clothing thermal insulation in mild cold (19 °C air), clothing thermal insulation should be taken into consideration. During the mild cold exposure, a slight decrease in rectal temperature ( $T_{re}$ ) was observed in both sexes but there were no significant differences related to clothing types and sex. During the mild cold exposure,  $T_{sk}$  (skin temperature) decreased by an average of male 2.0 °C (female 1.9 °C) and male 1.1 °C (female 1.5 °C) in the S- (short sleeves and knee trousers) and L-type (long sleeves and long trousers) clothing, respectively [57].

## 9. How PCMs works in textiles

Before applying PCM's to textile structure, the PCM's would be encapsulated in very small spheres to contain them while in a liquid state. These microcapsules have approximate diameters of between 1 μm and 30 μm. The microcapsules are resistant to mechanical action, heat and most types of chemicals. They react to temperature fluctuations in the following way [16]:

The temperature rises: when temperature rises due to a higher ambient temperature, the microcapsules react by absorbing heat. The PCMs in the microcapsules melt. They draw heat from their surroundings and store the surplus energy.

The temperature falls: when the temperature falls due to a lower ambient temperature, they release the previously stored heat. Interacting textiles structure with PCM micro-

capsules for garment applications, the following thermal benefits are realized [16]:

- a cooling effect, caused by heat absorption of the PCM
- a heating effect, caused by heat emission of the PCM
- a thermo-regulating effect, resulting from either the heat absorption or heat emission of the PCM which is used to keep the temperature of a surrounding substrate nearly constant.
- An active thermal barrier effect, resulting from either heat absorption, or heat emission of the PCM which regulates for instance, in a garment system the heat flux from the human body into the environment and adopts it to the thermal needs (i.e. activity level, ambient temperature).

The treated fabric with 22.9% add-on of microcapsules is capable of absorbing 4.44 J/g of heat if the microcapsules (melamine-formaldehyde microcapsules containing eicosane were manufactured by *in situ* polymerization) on the fabric undergo a melting process. The heat of absorption by the microcapsules delays the microclimate temperature increase of clothing. This leads to enhanced thermo-physiological comfort and prevents heat stress [58].

The impact of phase-change materials (PCM) on intelligent thermal-protective clothing has been investigated by Wang et al. [59]. In the heating process, when the PCM layer's temperature increases above the PCM's melting point (28.0 °C), the PCM melts and becomes liquid. During this process, thermal energy is absorbed and stored. After all the PCM becomes liquid, the temperature continually increases. When the PCM layer's temperature reaches 29.0 °C, the conductive fabrics were powered off. The temperature of the PCM layer then decreases after a short time. When the temperature of the PCM layer decreases below 27.0 °C, the liquid PCM becomes solid and releases heat energy. In this process, the PCM acts as a thermal buffer material by releasing stored heat. The electrical energy consumed by the clothing assembly (nonwoven fabric coated with PCM and having conductive layer) with PCM is about 30.9% less than that consumed by the clothing assembly without PCM (nonwoven fabric, having conductive layer). Therefore concluded that a conductive fabric can significantly increase the temperatures of the different layers of the assembly and make the assembly warmer.

## 10. PCM and clothing comfort

Comfort is a term created by psychologists; nevertheless it has a physiological basis which is far from clear [60]. Comfort is usually considered to be identical with the term optimum temperature, but even this term is identified differently by physiologists, behavioral scientists and those using biophysical techniques. Thermal comfort and discomfort rely upon both internal (core) and external (skin) temperature sensitivity and the central integration of these

two loops. When dealing with textile and allied assemblies, as in clothing or bedding, we are dealing with the factors contributing mainly to the external loop of the thermal comfort sensation. Skin has a special role, as it is not only the source of information by virtue of comfort sensors, but the interface between the thermal core of the body and the environment. The human body attempts to maintain core body temperature around 37 °C. The balance between perspiration and heat productions by the body and loss of the same is the comfort factor [61]. The body would be in a state of comfort when the body temperature is about 35 °C and there is no moisture on the skin.

Heat loss by evaporation is the only way to dissipate heat from the body when environment temperature is greater than skin temperature [62]. PCMs can be incorporated in a numerical three-node fabric ventilation model to study their transient effect on body heat loss during exercise when subjected to sudden changes in environmental conditions from warm indoor air to cold outdoor air. The results indicate that the heating effect lasts approximately 12.5 min depending on PCM percentage and cold outdoor conditions. Heat released by PCMs decreases the clothed-body heat loss by an average of 40–55 W/m<sup>2</sup> for a one-layer suit depending on the frequency of oscillation and crystallization temperature of the PCM. The experimental results reveal that under steady-state environmental conditions, the oscillating PCM fabric has no effect on dry resistance, even though the measured sensible heat loss increases with decreasing air temperature of the chamber [63].

## 11. How to incorporate PCMs in textiles

The PCMs change phases within a temperature range just above and below human skin temperature would be suitable for application in textiles. This interesting property of PCMs would be useful for making protective textiles in all-season. Fiber, fabric and foam with PCMs could store the heat body creates then release it back to body, as it needs. Since the process of phase change is dynamic; therefore, the materials are constantly changing from a state to another depending upon level of physical activity of the body and outside temperature. The thermo-regulating characteristic is possible in manmade fiber by adding PCM microcapsules to a polymer solution prior to fiber extrusion. In the process, PCM microcapsules are integrated inside the fiber itself. Coating, lamination, finishing, melt spinning, bi-component synthetic fiber extrusion, injection molding, foam techniques are some of the convenient processes for PCMs' incorporation into the textile matrix.

### 11.1. Fiber technology

The incorporation of PCM within a fiber requires first that the PCM be microencapsulated. PCMs would be added to the liquid polymer, polymer solution, or base

material and fibre is then spun according to the conventional methods such as dry or wet spinning and extrusion of molten polymer. The microencapsulated PCM fibers could store heat over long periods. If the environmental temperature drops, the fiber slowly radiate heat.

The composition and properties of a series of sheath/core composite polypropylene fibres nonwovens with different phase change material (PCM) contents in the core have been studied using SEM, DSC and temperature sensors [64]. It is observed that the PCM content in the fibre, sheath/core ratio and the content of 4-hole spiral crimp PET fibre affect the temperature regulating ability of the nonwoven. The temperature regulating ability has no truck with the fibre titer in the experimental scale. There can be a maximum temperature difference of 9.3 °C between the nonwovens made from composites and control (polypropylene) fibres during temperature rising, and 10.2 °C between control and composite samples during temperature dropping. Photothermal conversion and thermo-regulated fibres (PCTFs) have been prepared using the fibre-forming polymer containing photothermal conversion ceramic as sheath and the fibre-forming polymer containing microPCMs as core. It is observed that the photothermal conversion and thermo-regulated fibres have better temperature-regulating abilities when compared with the control. The maximum heat absorbing and heat releasing temperature differences are found to be 4.5 °C and 6.5 °C respectively when the PCTF nonwoven is compared with PP nonwoven [65].

### 11.2. Coatings

A coating composition for textiles includes wetted microspheres containing a phase change material dispersed throughout a polymer binder, a surfactant, a dispersant, an antifoam agent and a thickener. Preferred phase change materials include paraffinic hydrocarbons. The microspheres may be microencapsulated. To prepare the coating composition, microspheres containing phase change material are wetted and dispersed in a dispersion of water solution containing a surfactant, a dispersant, an antifoam agent and a polymer mixture. The coating would be then applied to a textile substrate. In an alternative embodiment, an extensible fabric would be coated with an extensible binder containing microencapsulated phase change material to form an extensible, coated fabric [24]. PCM could be incorporated into the textiles by coating using polymer such as acrylic, polyurethane, etc, and applied to the fabric. There are various coating processes available such as knife-over-roll, knife-over-air, pad-dry-cure, gravure, dip coating, and transfer coating.

### 11.3. Lamination

In order to improve thermo-physiological wearing comfort of protective garments, PCM would be incorporated into a thin polymer film and applied to the inner side of

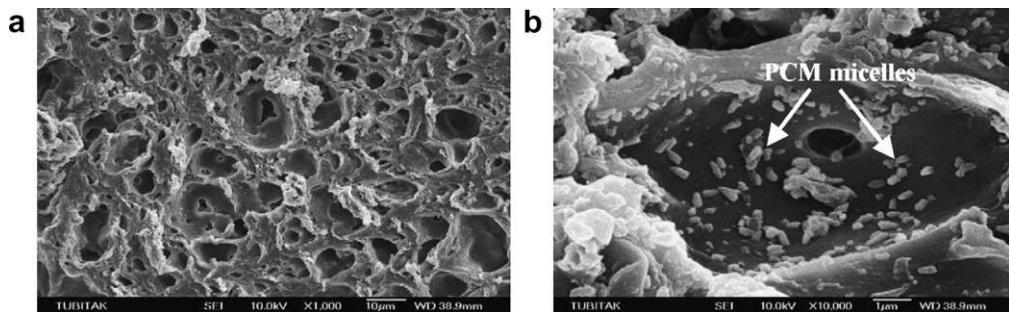


Fig. 5. PU1 containing *n*-hexadecane: (a) magnification 1000 $\times$ ; 10.0 kV and (b) magnification 10,000 $\times$ ; 10.0 kV (reproduced with permission from [68]).

the fabric system by lamination. The cooling effect of the PCM can delay the temperature rise and, hence, the moisture rises in the microclimate substantially. As a result, the wearing time of the garments can be extended significantly without the occurrence of heat stress as a serious health risk. The longer wearing times will further lead to a significantly higher productivity. The more comfortable wearing conditions will also result in a reduced number of accidents and lower error rates. Beside chemical protective suits the PCM can also improve the thermo-physiological wearing comfort of other protective garments made of nonwovens such as surgical gowns, uniforms, or garments worn in clean rooms [66,67]. Microcapsules would be mixed into a water-blown polyurethane foam mix and these foams are applied to a fabric in a lamination process, where the water is taken out of the system by drying process. The excellent honeycomb structure obtained during foam formation made considerable amount of still air trapping possibility, thus, leading to an increased passive insulation. Although the presence of PCM micelles in cells can easily be distinguished (Fig. 5) [68].

## 12. Microcapsulation

Microencapsulation of liquids and solids is an innovative micropackaging technology which is opening up new technical textiles which can provide textiles with new properties and added value [69,70]. Microencapsulation involves the production of microcapsules which act as tiny

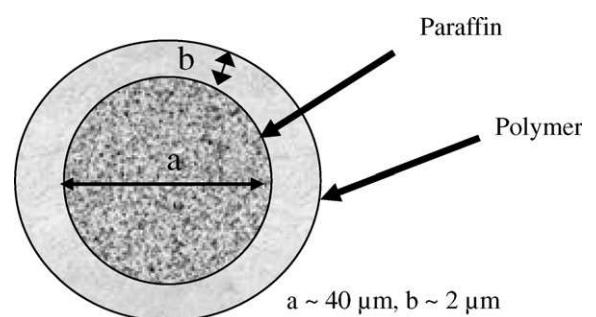


Fig. 6. Microencapsulation: Paraffinic PCM core material individually with a hard polymeric shell.

containers of solids. Microcapsules that have walls less than 2  $\mu\text{m}$  in thickness and 20–40  $\mu\text{m}$  in diameter (Fig. 6) is useful in fiber applications [2]. These containers release their core contents under controlled conditions to suit a specific purpose. The microcapsules are produced by depositing a thin polymer coating on small solid particles or liquid droplets, or on dispersions of solids in liquids. The core contents—the active substance—may be released by friction, by pressure, by diffusion through the polymer wall, by dissolution of the polymer wall coating, or by biodegradation. In their application in textiles, the paraffins are either in solid or liquid state. In order to prevent the paraffin's dissolution while in the liquid state, it is enclosed into small plastic spheres with diameters of only a few micrometers. These microscopic spheres containing PCM

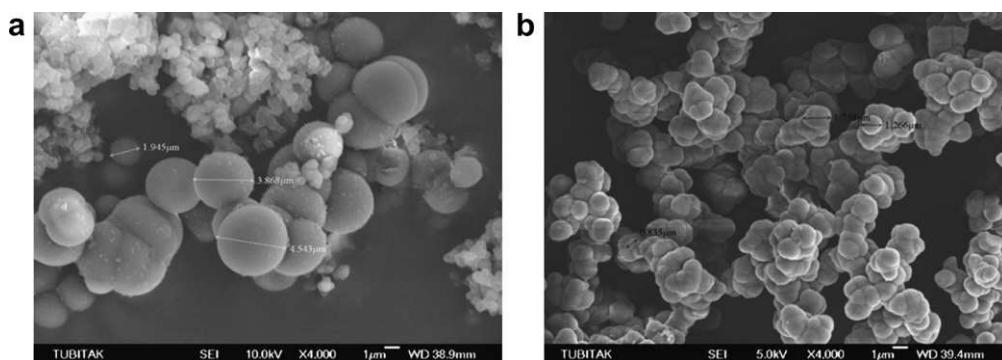


Fig. 7. (a) Polyurea-formaldehyde microcapsules containing *n*-octadecane core; magnification 4000 $\times$ ; 10.0 kV. (b) Polyurea-formaldehyde microcapsules containing the mixture of *n*-octadecane and PEG 600 core; magnification 4000 $\times$ ; 5.0 kV (reproduced with permission from [71]).

are called PCM-microcapsules. The microencapsulated paraffin is either permanently locked in acrylic fibres or in polyurethane foams or coated onto the surface of a textile structure.

Microcapsule production may be achieved by means of physical or chemical techniques. The use of some techniques has been limited to the high cost of processing, regulatory affairs, and the use of organic solvents, which are concern for health and the environment. Physical methods are mainly spray drying or centrifugal and fluidized bed processes which are inherently not capable of producing microcapsules smaller than 100 µm. The most suitable chemical processes are associated with the simple or complex coacervation and interfacial (or *in situ*) polymerization techniques [71]. The microencapsulation method based on *in situ* polymerization technique, was quite successful to produce microcapsules (Fig. 7) with an enhanced thermal capacity in relation to the PCM content. Seventy-seven percent of microcapsules were obtained  $\leq 100$  µm in diameter and 90% of them were smaller than 185 µm by using *in situ* polymerization techniques.

### 13. Smart temperature adaptable textiles

The required thermal insulation of clothing systems primarily depends on the physical activity and on the surrounding conditions, such as temperature and relative humidity. The quantity of heat produced by human being depends very much on the physical activity and can vary from 100 W while resting to over 1000 W during maximum physical performance [62]. Particularly during the cooler seasons (approx. 0 °C), the recommended thermal insulation is defined in order to ensure that the body is sufficiently warm when resting. At a more intensive activity, which is often the case with winter sports, the body temperature increases with enhanced heat production. To keep this increase within a certain limit, the body perspires in order to withdraw energy from the body by evaporative cooling. If the thermal insulation of the clothing is reduced during physical activity, a part of the produced heat can be removed by convection thus the body is not required to perspire so much. The quality of insulation in a garment against heat and cold will be extensively governed by the thickness and density of its component fabrics. High thickness and low density improve insulation due to the presence of lots of air gaps. However, a garment made from a thick fabric will have greater weight, and the freedom of movement of the wearer will be affected. The effectiveness of the insulation is also affected by the external temperature. The more extreme the temperature, be it very high or very low, the less effective the insulation becomes. Clearly then a garment made from an intelligent fabric whose nature can vary depending on the external temperature can provide superior protection. Thermo-regulated textiles are a kind of smart new textile product that contains low temperature phase-change materials (PCM). When a substrate containing PCM is heated, the increases

in temperature of the substrate is interrupted at the melting point of the phase change material, due to absorption as latent heat. The temperature will rise only when the entire solid has melted. Conversely, during the cooling process at low ambient, the drop in temperature is interrupted at the solidification temperature. The heat flux through a material containing PCM is thus delayed in both heating as well as cooling, during the process of phase change. This thermal insulation is dependent on temperature and time; and being temporary in nature, it can be termed dynamic thermal insulation [61]. Fabrics have been given enhanced thermal properties by coating the fibers with phase change material and plastic crystals. Temperature adaptable textile fibers [72] which store heat when the temperature rises and release heat when the temperature decreases, in which phase change or plastic crystalline materials would be enclosed within hollow fibers, or impregnated upon non-hollow fibers. At the phase change temperature, a characteristic of phase change material during the heating cycle is to absorb and hold a quantity of thermal energy at almost a constant temperature while changing to the next phase. Thus, the material can be precooled and used as a barrier to heat, since a quantity of thermal energy must be absorbed by the phase change material before its temperature can rise. The phase change material may also be preheated and used as a barrier to cold, as a quantity of heat must be removed from the phase change material before its temperature can begin to drop.

Nonwoven protective garments are used in a variety of applications such as asbestos and lead abatement, pest control, and treatment of hazardous waste. The construction of the nonwovens used in such garments provides a high barrier function against the penetration by dust, liquids, or gases. However, in the same way the fabric system prevents the transfer of hazardous materials into the garment, it also limits the outward passage of body heat and moisture. As a result, under strenuous activities, the core temperature of the wearer's body may rise quickly above the comfort level into the heat stress zone. The problem can be solved by applying phase change material. The incorporation of phase change material in a nonwoven fabric system adds a thermo-regulating feature to it. By using such nonwoven fabric systems with incorporated phase change material for protective garments, the wearer's comfort can be enhanced substantially and the occurrence of heat stress could be prevented [67].

### 14. Testing of PCM incorporated textiles

The melted and unmelted morphology of PCM could be identified by polarized optical microscopy (POM) [73]. POM revealed that before copolymer's transition temperature, with the increase of temperature, the spherulites had no change; when the temperatures approached transition point, the spherulites faded away and eventually disappeared. Differential scanning calorimetry measurements would be used to determine the thermal capacities, melting

temperature of PCM, and crystallization temperature of the phase changes of PCM microcapsules embedded in textile structures. On the other hand thermo-regulated properties of PCM containing textiles could be measured by surface cooling rate measurements. The indices of thermal regulating capability ( $I_d$  and  $\Delta_{td}$ ), static thermal insulation ( $I_s$ ), and the thermal psychosensory intensity (TPI) of textile incorporating phase change materials can be measured by an instrument that is called the Fabric Intelligent Hand Tester (FIHT) [74]. The index of static thermal insulation ( $I_s$ ) can be obtained from the test data by calculating the mean heat flux at the equilibrium state. The indices of the thermal regulating capability ( $I_d$  and  $\Delta_{td}$ ) can be obtained by calculating the differences between the heat flux changes of PCM and non-PCM fabrics.

## 15. Applications of PCMs incorporated textiles

Phase change materials (PCMs) in textiles adapt to the thermal regulating functional performance of PCM garments [75,76] by altering their state of aggregation in a defined temperature range. Applications of phase change textiles include apparel, blankets, medical field, insulation, protective clothing and many others. The following is a brief summary of the application of PCM in textile fields.

### 15.1. Space

The technology uses phase change materials, which were first developed for use in space suits and gloves to protect astronauts from the bitter cold when working in space. Phase-change materials keep astronauts comfortable at space.

### 15.2. Sports wear

From original applications in space suits and gloves, phase change materials (PCM) are nowadays using in consumer products as well. In order to improve the thermal performance of active-wear garments, clothing textiles with thermo-regulating properties are widely used. The thermo-regulating effect provided by these textiles could be based on the application of PCM. It is necessary to match the PCM quantity applied to the active-wear garment with the level and the duration of the activity for the garment use. Active wear needs to provide a thermal balance between the heat generated by the body and the heat released into the environment while engaging in a sport. The heat generated by the body during sports activity is often not released into the environment in the necessary amount thus increasing thermal stress. When phase change materials would incorporate in sports wear, during physical activity, the wearer's excessive body heat increases and is absorbed by the encapsulated phase change materials and released when necessary. Snowboard gloves, underwear, active wear, ice climbing and underwear for cycling and

running are few more examples of applications of PCMs in sports wear.

### 15.3. Bedding and accessories

Embedded microcapsules into quilts, pillows and mattress covers ensure active temperature control in bed. When the body temperature rises, the additional heat energy is absorbed and the body cools down. When the body temperature drops, the stored energy is released and the body is kept warm.

### 15.4. Medical applications

As the phase change materials interact with the microclimate around the human body, responding to fluctuations in temperature which are caused by changes in activity levels and in the external environment. Therefore, the textiles treated with PCM microcapsules have potential applications in surgical apparel, patient bedding materials, bandages and products to regulate patient temperatures in intensive care units [74]. PEG-treated fabric may be useful in medical and hygiene applications where both liquid transport and antibacterial properties are desirable, such as surgical gauze, nappies and incontinence products. Heat-storage and thermo-regulated textiles can keep the skin temperature within the comfort range, so they can be used as a bandage and for burn and heat/cool therapy [77].

### 15.5. Shoes and accessories

Currently, PCMs are also used in footwear, especially ski boots, mountaineering boots, race car drivers' boots etc. The phase change technology reacts directly to changes in temperature of both the exterior of the garment and the body. Phase change materials (paraffins) contained in microcapsules are linked to a specific temperature range depending on end use (36 °C for a motor cycle helmet and 26 °C for gloves). Heat-storage and thermo-regulated textiles can absorb, store, redistribute and release heat to prevent drastic changes in the wearer's head, body, hands and feet. In the case of ski boots, the PCM absorbs the heat when the feet generate excess heat, and send the stored heat back to the cold spots if the feet get chilly. This keeps the feet comfortable. Ski boots, footwear and golf shoes are some of the products where PCM could be used [77].

### 15.6. Other

PCMs are used in automobile textile such as seat cover. Automobile interior applications use paraffins due to their high capacity for heat storage; lack of toxicity, corrosiveness, or hygroscopic properties; low cost; and amenability to mixing to realize the desired temperature range. The paraffins are microencapsulated and applied to a textile matrix. PCM treated fabric in headliners and seats

provided superior thermal control. Helmets, fishing waders, firefighters' suits, are some other examples of application of PCMs in textiles.

## 16. Market for PCM in textile applications

From original applications in space suits and gloves, phase change materials (PCM) are in consumer products, nowadays. Microencapsulation of liquids and solids is an innovative micropackaging technology which is opening up new marketing opportunities for performance apparel markets for making smart thermo-regulated textiles. In textile processing, specially in the nonwovens business, micro-encapsulated PCM are on the market already [66]. A narrow interpretation of smart textiles or smart materials is when it shows a clearly defined reaction as a result of a clearly defined stimulus. This namely holds good for all smart textiles. Solutions were generated from the conclusions drawn from innovation management and marketing. The only appropriate definition says that something is new if it has been categorized as something new by the market [78]. Such textiles have integrated technology or have new junctions or capabilities. Applications range from the highly complex life support systems to the convenient or fun, and from life saving military uniforms to stain resistance or entertainment. The main areas of focus for smart and interactive textiles are the military, healthcare, and performance sportswear. Definitely, PCM incorporated textile would take a major role in future smart textiles segments. In today's competitive market situation in world, the demand of today's customer is to get comfort in cloth, which is to be worn in different situations from daily wear to functional wear. Phase change materials are the source to be incorporated in textile material to add value i.e. comfort to wearer [79].

## 17. Challenges and opportunities

Phase change materials found in today's consumer products originally were developed for use in space suits and gloves to protect astronauts from extreme temperature fluctuations in space. There are many challenges facing the use of this new innovative material. The use of innovative new materials and integration of PCM into garments requires, for example, the development of new types of testing methods and standards. Furthermore, the development of materials, such as their mechanical properties, durability or functionality in various conditions, may take a long time. The main challenge in developing textile-PCM structures is the method of their application. Encapsulation of PCMs in a polymeric shell is an obvious choice but it adds dead weight to the active material. Efficient encapsulation, yield of encapsulation, stability during use and integration of capsules onto fabric structure are some of the technological issues would be considered. Another important challenges lies to the textile community for this innovative

textile in practical use is the durability of PCM incorporated textiles in repeated uses.

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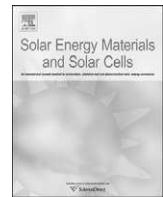
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## A temperature-regulating fiber made of PEG-based smart copolymer

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### ABSTRACT

A poly(ethylene glycol) (PEG)-based thermoplastic shape memory polyurethane was synthesized via bulk polymerization. The corresponding fiber, as a temperature-regulating fiber, was fabricated via melt spinning. The prepared 100-dtex fiber had a tenacity of 0.7 cN/dtex and breaking elongation of about 488%. The fiber's phase change behaviors, crystalline morphology, dynamic mechanical properties, and temperature-resistant performance were investigated using polarizing optical microscopy, differential scanning calorimetry, dynamic mechanical analysis, and thermogravimetry. The PEG soft segment phase transfer between crystalline and amorphous states resulted in heat storage and release. The hydrogen-bonded hard segment phase, serving as 'physical cross-links,' restricted the free movement of soft segments, hence at temperatures above the PEG phase melting transition, the fiber still possessed certain mechanical strength. The differential scanning calorimetry results indicated that the fiber had large latent heat-storage capacity of about 100 J/g with a crystallizing temperature of 20.9 °C and a melting temperature of 44.7 °C. The dynamic mechanical analysis results showed that the fiber has a plateau elastic modulus in the region above the PEG phase melting transition and below 160 °C. The thermogravimetry results suggested that the fiber had a much broader applicable temperature range compared to pure PEG. The thermo-mechanical cyclic tensile testing results showed that the fiber had good shape memory effect with the shape fixity ratio more than 85.8% and the recovery ratio above 95.4%.

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### 1. Introduction

Human body has the most comfortable temperature at every part of skins. When the temperature of the skin differs more than 3.0 °C from this ideal temperature, the human body feels uncomfortable [1,2]. One of the primary purposes of clothing design is to protect the wearer skin temperature from rising or falling too far. It would be most ideal if, at high temperature, the excess heat a person produces could be stored in the clothing system and then released again when he starts to get chilly. Phase change materials (PCMs) that have been used to regulate temperature fluctuations have this function. When the temperature is above the phase change temperature, PCMs absorb and store heat energy with no temperature increase. When the material cools down, the latent heat is released to the human body. In the temperature-regulating clothing system, the phase transition temperature should be in the range of 10–50 °C [3–7]. The phase change temperature of hydrated inorganic salts, polyhydric alcohol mixture (water solution), polyethylene glycol (PEG), polytetramethylene glycol (PTMG), aliphatic polyester, linear chain hydrocarbon, hydrocarbon alcohol, and hydrocarbon

acid is in this interval [8–11]. Temperature-regulating fabrics containing PCMs can be used not only in apparel and home textiles but also in technical textiles.

Many research groups have tried to prepare temperature-regulating fibers by incorporating microencapsulated PCMs into fibers via wet or melt spinning [12–16]. This method shows several disadvantages: first, microcapsules have the potential to form clusters and cause discontinuity in the spinning process; secondly, the thermal capacity of the prepared fiber is rather modest, about 8–12 J/g, because the microencapsulated PCMs have an upper loading limit [16]; in addition, it is more complex to incorporate PCMs into melt-spun fibers, because PCMs are mostly volatile materials, which are not fit for high-temperature extrusion and pumping process.

PEG is a well-studied solid-liquid phase change polymeric material. It has a melting temperature of around 3.2–68.7 °C and a very high phase change enthalpy depending on its molecular weight [2,6,17]. However, it exhibits unreliable and poor thermal behavior on repeated thermal-cool cycles [16,18,19]. Solid-solid PCMs absorb and release heat in the same manner as solid-liquid PCMs; however, these materials do not change into a liquid state at above the phase change temperature. They merely soften or harden with temperature change above and below the phase change temperature. As a result, they show several advantages over other solid-liquid PCMs: no liquid or gas generation, small

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volume change, and no seal needed [20–22]. Several research groups have made great efforts to prepare solid–solid PCMs by employing PEG as phase change ingredient while using another skeleton-forming ingredient to keep the material in solid state after the melting of PEG.

Zhang et al. [11,23] prepared composite fibers of PEG/PP, PET, or ethylene-vinyl acetate by controlling suitable spinning parameters and component contents. However, this kind of materials prepared via physical blending has a tendency to lose its phase change characteristics after several heating–cooling cycles due to the loss of PEG. Hu et al. [24] prepared a solid–solid PCM by copolymerizing poly(ethylene terephthalate)–PEG. However, even the maximum enthalpy, which is 26.85 J/g at 45 wt% PEG content, was still much lower in comparison with that of pure PEG. Jiang et al. [25] developed a network solid–solid PCM with rigid polymer cellulose diacetate (CDA) serving as a skeleton, and the PEG as a branch chain. However, because of the covalent network structure of the PEG grafted CDA, the material is not fit for fiber preparation. More recently, Li and Ding [26] prepared a novel PEG/MDI (diphenylmethane diisocyanate)/PE (pentaerythritol) cross-linking copolymer via the condensation reaction of PEG with tetrafunctional pentaerythritol isocyanate. The phase transition enthalpy was more than 100 J/g with a transition point at 58.68 °C. However, this material was prepared by solution polymerization and using dimethylformamide (DMF) as solution, which is harmful for environment and human body. In addition, the material has the same problem of not fitting for fabricating fibers.

Thermoplastic shape memory polyurethanes are linear chain segmented block smart copolymers. These polyurethanes may be synthesized from three starting materials: long-chain polyol, diisocyanate, and chain extender. Diisocyanate and chain extender form the hard segment. The long-chain polyol forms the soft segment [27]. The shape memory effect of the shape memory polyurethane fiber is because of the so-called micro-phase-separated heterogeneous structure composed of hard segment phase and soft segment phase. The shape memory polyurethane fiber is processed to have a permanent ‘parent’ length. This permanent length is stored in the system while the polymers assume different temporary lengths, and by heating the polymers to higher than the switch transition temperature, the permanent length can be restored sharply [28–33]. The ‘molecular switch’ to freeze temporary length may be the melting [30,34] or a glass transition of soft segment phase or a mixed glass transition temperature of soft segment and hard segment phase [33,35–39]. Thermoplastic shape memory polyurethanes can be processed using wet, dry, or melt spinning [28,31,33,40–44].

In the work by employing PEG as soft segment, we prepared a shape memory polyurethane fiber with diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) as hard segment by bulk polymerization and melt spinning. The fiber’s phase change behaviors, crystalline morphology, dynamic mechanical properties, and temperature-resistant performance were investigated

using polarizing optical microscopy, differential scanning calorimetry, dynamic mechanical analysis, and thermogravimetry. The shape memory effect was investigated using thermo-mechanical cyclic tensile testing since shape memory polyurethanes have found broad applications in textiles, automotive parts, building and construction products, intelligent packing, implantable materials, sensors, and actuators. This temperature-regulating fiber possessing shape memory effect together may find more applications in the near future.

## 2. Experimental

### 2.1. Material

The PEG-based linear chain polyurethane was synthesized using PEG-3400 (International Laboratory, USA) as soft segments, and MDI (Sigma-Aldrich, Inc.) and BDO (Sigma-Aldrich, Inc.) as hard segments via bulk polymerization. The schematic synthesis route is shown in Fig. 1. All glass vessels were cleaned and heated in a muffle to remove all moisture and organic residual before use. All chemicals were demoistured prior to use. Polyurethane was prepared by the pre-polymerization technique [45,46]. Prepolymers were obtained by terminating PEG with excessive MDI on both ends at 80 °C for half an hour. BDO was added at last and the reaction was controlled at below 90 °C for 5 min. To make polyurethane with linear macromolecules, the mole ratio ( $[NCO]_{MDI}/[OH]_{BDO}+[OH]_{PEG}$ ) was 1:1 strictly. All the reactions took place in a highly pure nitrogen environment. Polyurethane pellets were prepared using a single extruder. Then the pellets were cured in a vacuum oven at 110 °C for 1 day.

### 2.2. Molecular weight testing

Weight average molecular weight (MW) and number average molecular weight (MN) of the prepared polyurethane were determined with a multiangle laser light scattering apparatus (DAWN-DSP, Wyatt Technology Co., Santa Barbara, CA) combined with a P100 pump (Thermo Separation Products) equipped with a TSKGEL G5000 HHR column (7.8–300 mm) and an Optilab<sup>®</sup> rEX refractive index detector. The solvent used was high-performance liquid chromatograph grade DMF (Ajax Finechem) at 25 °C. The refractive index increment ( $dn/dc$ ) of polyurethane in DMF was measured with a double-beam differential refractometer (DRM-1020, Otsuka Electronics Co., Japan). Astra software was used for data analysis.

### 2.3. Melt flow index

The melt flow index of the polyurethane was tested with a Davenport melt flow indexer MFI-10 (Fareham, UK). The samples were pre-heated in a barrel held at a set temperature for 6 min.

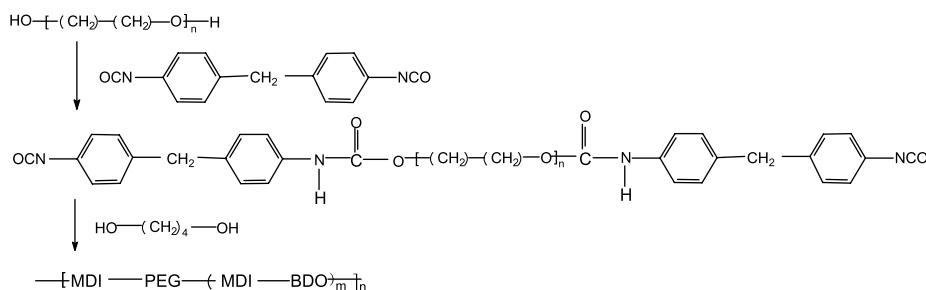


Fig. 1. Synthetic scheme of the PEG polyurethane.

The amount of the polymer fed into the extruder was about 2.16 kg. The test was conducted five times at every testing temperature.

#### 2.4. Melt spinning

Before spinning, the polyurethane was dried in a vacuum oven to reduce polymer moisture content to less than 100 ppm tested using a Micro-water Analyzer CHY-8 (Donghua University, China). The temperature-regulating fiber was spun using a self-fabricated laboratory spinning machine with highly pure nitrogen protection at 210 °C. Polyurethane fibers of 100 dtex were prepared. The fibers are named temperature-regulating shape memory fiber (TRSMF). The monofilament surface image was taken with a Leica Stereoscanner 440 scanning electron microscope (Cambridge, UK) operating at 20 kV.

#### 2.5. Mechanical property

Mechanical properties were measured with Instron 4411 (Instron Corporation of USA) according to the ASTM D2256 standard. The sample gauge length between clamps was 20 mm and the stretching speed was 300 mm/min. The test was conducted at room temperature (22 °C) five times.

#### 2.6. Polarizing optical microscopy

A Leitz wetzlar polarizing optical microscope (Ernst Leitz Wetzlar, Germany) equipped with a Mettler FP 80 hot stage and a controller were used to observe the morphologies of PEG and TRSMF. A digital camera (Pixera camera of Pixera Corporation of Japan) was used to capture images in converging white light with analyzer and polarizer crossed. The fiber cross-section was obtained by using microtome. First, a monofilament was embedded in epoxy resin 1 day before test. After the epoxy was completely hardened, it was microtomed in the fiber transverse direction with a diamond knife (Micro Star Co.) and a Reichert-Jung Ultracut microtome (at room temperature; Heidelberg, Germany).

#### 2.7. Differential scanning calorimetry

The thermal properties of pure PEG and the TRSMF were determined using a differential scanning calorimeter (Perkin-Elmer Diamond Differential Scanning Calorimeter) with nitrogen as purge gas. Indium and zinc were used for calibration. First, samples were heated from 0 to 100 °C at a 1 °C/min heating rate and kept at 100 °C for 1 min, and subsequently cooled to 0 °C at the cooling rate of 1 °C/min and kept at 0 °C for 1 min. Then, the sample was reheated at the same heating rate to 100 °C. The above cycle was repeated five times. The heat flow change with increasing temperature was recorded.

#### 2.8. Dynamic mechanical analyses

Dynamic mechanical analysis test was carried out on a Perkin-Elmer Diamond Dynamic Mechanical Analyzer operated in a tensile mode. The heating rate was 2 °C/min; the frequency was 2 Hz, and the oscillation amplitude was 5.0 μm. The dynamic mechanical analysis test was conducted over the temperature range –100 to 200 °C. The gauge length between the clamps was 15 mm. The modulus was usually calculated by determining the cross-sectional area and the strain caused for the force employed in testing the specimens. If the cross-section area is used in the calculation of stress and modulus, then the units will be GPa or

MPa. However, the cross-section area of TRSMF, which was not strictly regular, was difficult to measure. In this testing, the resulting data about the storage modulus were obtained by using linear density instead of cross-section area, similar to the calculation of fiber initial modulus in ASTMD2256. The unit of the storage modulus was N/dtex.

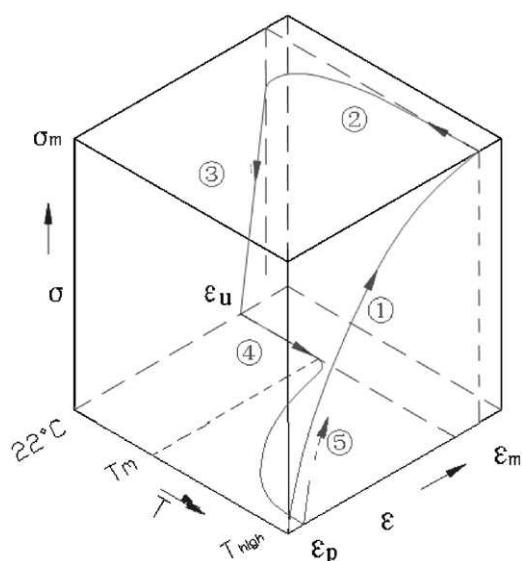
#### 2.9. Thermogravimetry

Thermogravimetry and derivative of thermogravimetry curves of pure PEG and TRSMF were obtained using a Netzsch TGA Instruments Co. thermal analysis system (STA449C). About 10 mg of the dried sample was weighed into an alumina crucible and the profiles were recorded at a heating rate of 10 °C/min in air atmosphere.

#### 2.10. Thermo-mechanical cyclic tensile testing

To quantify the smart fiber shape fixity ratio and recovery ratio, the thermo-mechanical cyclic tensile testing was conducted using tensile tester (Instron 4466) equipped with a self-fabricated temperature-controlled chamber. The sample gauge length was 20 mm. The cyclic tensile testing path is shown in Fig. 2;  $\varepsilon_m$  is the defined maximum deformation in the cyclic tensile testing. It is 100% strain for this study;  $\varepsilon_u$  is the strain after unloading at  $T_{low}$ , and  $\varepsilon_p(N)$  the residual strain after recovering in the  $N$ th cycle. The thermo-mechanical cycles for measuring the shape memory properties are as follows. (1) The fiber was first stretched to 100% elongation ratio at 60 °C ( $T_{high}$ ), which is above the switch transition temperature at a drawing speed of 10 mm/min [47,48]. (2) Subsequently, cool air was vented passively into the chamber to cool down the sample to 22 °C and the temperature was kept for 15 min to fix the temporary elongation. (3) Then upper clamp was returned to the original position at a speed of 40 mm/min and the fiber shrank from  $\varepsilon_m$  to  $\varepsilon_u$  because of instant elastic recovery. (4) Finally, the fiber was heated to 70 °C to allow shape memory recovery with the resulting fiber elongation returned to  $\varepsilon_p$ . (5) The second cycle began. The fixity ratio  $R_f$ , recovery ratio  $R_r$  at the  $N$ th cycle, and total recovery ratio  $R_{r,tot}$  after the  $N$ th cycle are calculated according to following equations [34,49]:

$$R_f(N) = \varepsilon_u(N)/\varepsilon_m \times 100\%$$



**Fig. 2.** Schematic thermo-mechanical cyclic tensile testing path.

$$R_{\text{tot}} = [\varepsilon_m - \varepsilon_p(N)]/\varepsilon_m \times 100\%$$

$$R_p(N) = [\varepsilon_m - \varepsilon_p(N)]/[\varepsilon_m - \varepsilon_p(N-1)] \times 100\%$$

### 3. Results and discussion

#### 3.1. Melt flow index

The obtained polyurethane had an  $M_w$  of  $2.45 \times 10^5$  and an  $M_n$  of  $1.65 \times 10^5$  with a polydispersity index 1.49. The melt flow index curve of the prepared polyurethane as a function of temperature is shown in Fig. 3. The melt flow behavior of the polyurethane is similar to that of a thermoplastic polymer. Melt flow index rises exponentially with increasing temperature. From Fig. 3, it can be preliminarily determined that the appropriate temperature of polyurethane melt spinning is about 210 °C. The surface image of the prepared TRSMF given in Fig. 4 shows that the prepared TRSMF surface is smooth and uniform.

#### 3.2. Mechanical property

The stress-strain curves of the TRSMF derived from the five experiments are shown in Fig. 5. The prepared 100-dtex fiber has a tenacity of about 0.7 cN/dtex, and the strain at break of 488%. The fiber shows obvious neck-type phenomena, which is frequently observed in crystalline polymer. The tenacity is acceptable for textile applications in most circumstances [50]. In comparison with most other man-made fibers such as polyester and nylon, the mechanical strength of TRSMF is lower. Polyester and nylon usually have high tenacity above 3.0 cN/dtex and low breaking elongation ratios. Their mechanical properties are attributed to their higher overall orientation, strong intermolecular bonding in polyamide, and high crystallinity of the molecular chain in polyester [51]. However, for the TRSMF, which shows high shape fixity ratios and shape recovery ratios, the elongation at break of the TRSMF is much higher compared to polyester and nylon.

In the segmented polyurethane system, the high molecular weight polyol (between 600 and 10,000) provides the polyurethane with high breaking elongation ratios, usually more than 400% and the hydrogen-bonded hard segments supply it with high mechanical strength. To obtain high heat-storage capacity of

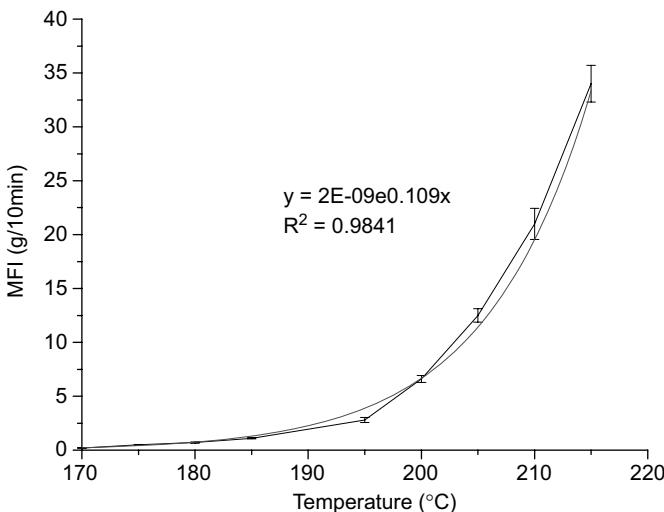


Fig. 3. Melt flow index of the prepared smart polyurethane with increasing temperature.

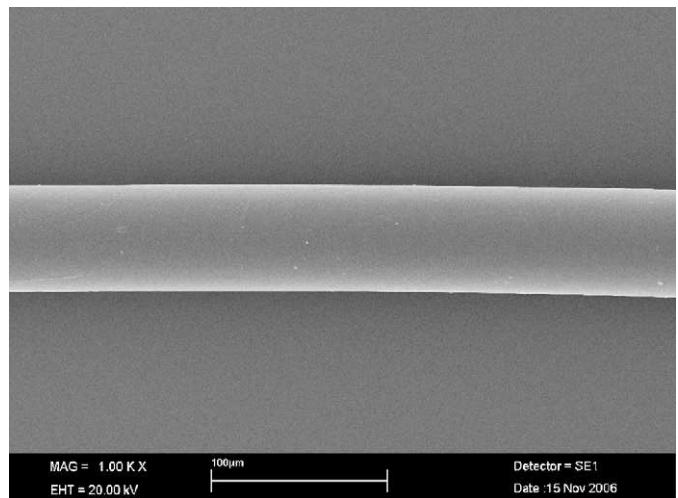


Fig. 4. SEM surface image of TRSMF.

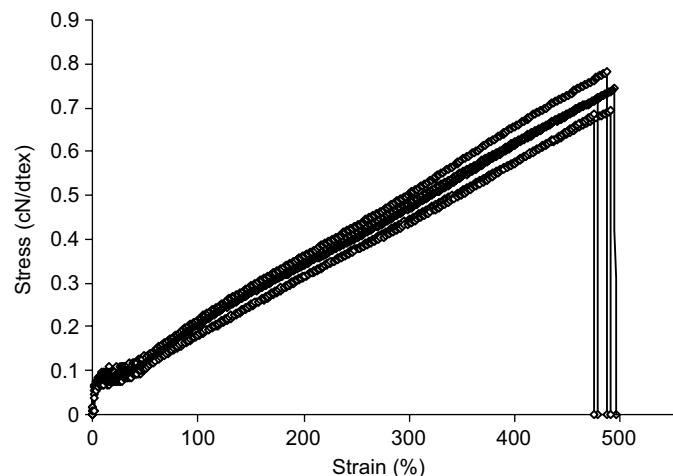
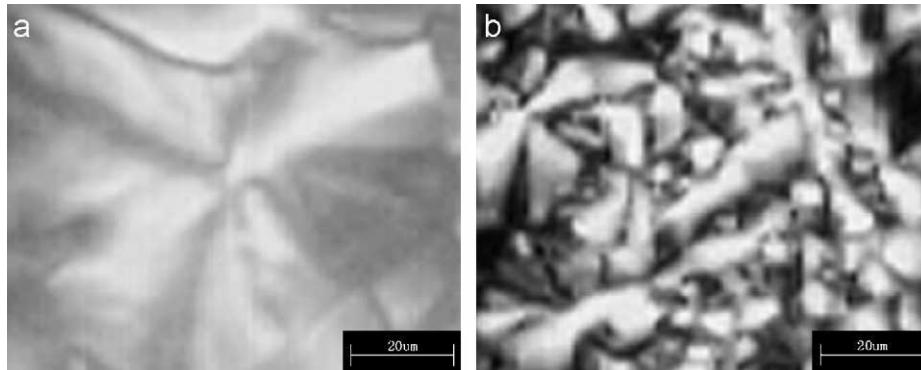


Fig. 5. Stress-strain curves of the TRSMF.

the TRSMF, the PEG segment content in the polyurethane system should be high, which reaches 80 wt% in this work. The fiber mechanical strength can be improved by decreasing the soft segment content; however, this is at the expense of TRSMF heat-storage capacity.

#### 3.3. Polarizing optical microscopy

The polarizing optical microscopy images of pure PEG and TRSMF at room temperature are given in Figs. 6(a) and (b) respectively. It can be seen that at room temperature, both pure PEG and TRSMF show crystalline cross-extinction patterns, which suggest that their crystals are spherulites. However, the spherulites in PEGPU are much smaller than, and not as perfect as those, in pure PEG. In Fig. 6(a), only one spherulite is observed, while in Fig. 6(b), in the same-size area, several crystals exist. In addition, many crystal fragments are observed in TRSMF polarizing optical microscopy image. This may be due to two reasons: first, in the polyurethane system, the hard segments intrude into the well-formed PEG phase and interfere with the PEG crystalline behavior; secondly, during the melt-spinning process and winding process, the spherulites of PEG phase in TRSMF are stretched and deformed in the fiber longitude direction and consequently the spherulites are destroyed to some extent. Therefore, the



**Fig. 6.** Polarizing optical microscopy images of (a) pure PEG and (b) TRSMF at room temperature.

spherulites in TRSMF are much smaller than, and not as perfect as those, in pure PEG.

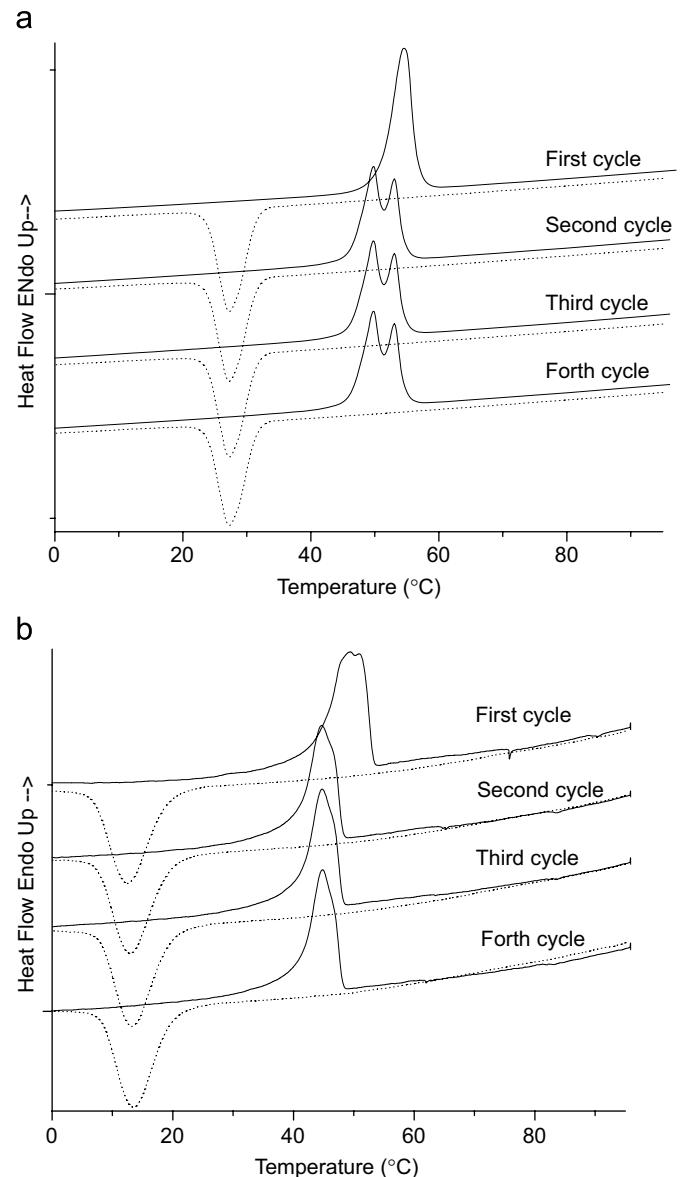
#### 3.4. Differential scanning calorimetry

The differential scanning calorimetry curves of the pure PEG and TRSMF are shown in Figs. 7(a) and (b). The melting temperature, crystallizing temperature, melting enthalpy, and crystalline enthalpy are tabulated in Table 1. The differential scanning calorimetry results in the first heating scan are different from those in the following cycles. This is attributed to the different thermal histories of the samples. The thermogram curves of pure PEG show an exothermic crystallization peak at 29.4 °C in the cooling scan and endothermic melting peaks in the second heating at 51.7 and 55.1 °C. Similarly, the thermogram curves of TRSMF display an exothermic crystallization peak at 20.7 °C in the cooling scan and an endothermic melting peak at 44.7 °C in the heating scan. The crystallizing and fusion enthalpy of TRSMF are about 100 J/g. Even though the crystallizing and fusion enthalpy of TRSMF are lower compared to that of pure PEG, its thermal transition enthalpy is much higher in comparison with those of most solid–solid PCMs reported previously [24–26,52].

As can be seen from Table 1, at ambient temperature, in the polyurethane system, the soft segments have high crystallinity. As a result, TRSMF is not as completely elastic as polyurethane spandex fibers such as Lycra, Fujibo, Glospan, and Mobilon [28,53–55].

#### 3.5. Dynamic mechanical analyses

The dynamic mechanical test of PEG oligomer could not be conducted because of its poor mechanical properties. The elastic modulus  $E'$  and loss tangent  $\tan \delta$  of the TRSMF over the temperature range –100 °C to 250 °C are presented in Fig. 8. At temperatures from –50 to 50 °C,  $E'$  has two sharp decreases and accordingly  $\tan \delta$  shows a peak change and a step change. The first decrease of  $E'$ , which emerges in the vicinity of –50 °C, can be ascribed to the glass transition of the soft segment PEG phase. The second decrease is because of the melting transition of the soft segment EPG phase at about 40 °C, which is more obvious in the TRSMF differential scanning calorimetry curves. At temperatures above 40 °C, when the soft segment crystals melt, the fiber does not break because of the hydrogen-bonded hard segments. At the plateau region, the elastic modulus of the fiber is completely attributed to the hard segments [56]. On heating above 160 °C, another decrease in  $E'$  is observed, indicating that the physical cross-linkings between the hard segments began to be destroyed [41,57,58].



**Fig. 7.** Differential scanning calorimetry curves of (a) pure PEG and (b) TRSMF (solid line: heating; dot line cooling).

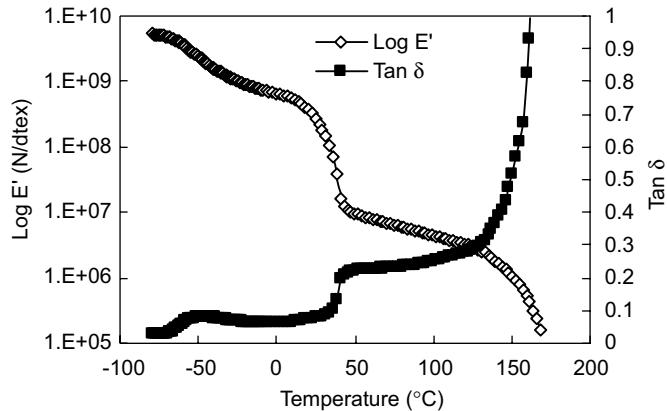
#### 3.6. Thermogravimetry analysis

Thermogravimetry was employed to assess the thermal resistance property of TRSMF. The obtained thermogravimetry

**Table 1**

	$T_m$ & $T_c$ (°C)	$\Delta H$ (J/g)	Crystallinity (%)
PEG-3400			
First cycle			
Heating	56.6	174.1	88.4
Cooling	29.3	158.8	80.6
Second cycle			
Heating	51.7/55.1	154.1	78.2
Cooling	29.4	158.9	80.7
Third cycle			
Heating	51.7/55.1	154.1	78.2
Cooling	29.5	159.0	80.7
Fourth cycle			
Heating	51.7/55.2	155.2	78.8
Cooling	29.5	160.0	81.2
TRSMF			
First cycle			
Heating	49.5	105	53.3
Cooling	20.4	82	41.6
Second cycle			
Heating	44.7	74	37.6
Cooling	20.9	83	42.1
Third cycle			
Heating	44.7	73	37.1
Cooling	21.3	85	43.1
Fourth cycle			
Heating	44.8	76	38.6
Cooling	21.5	87	44.2

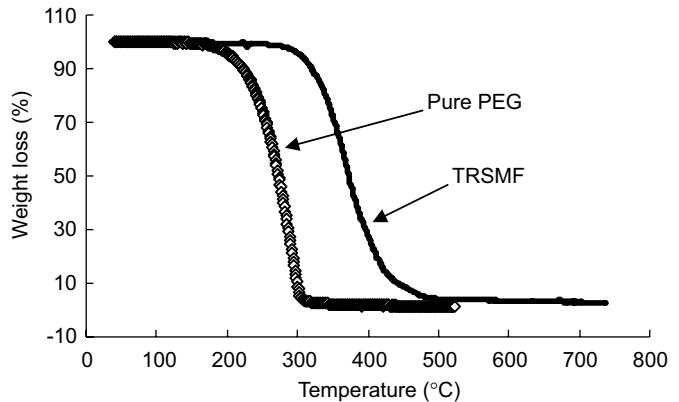
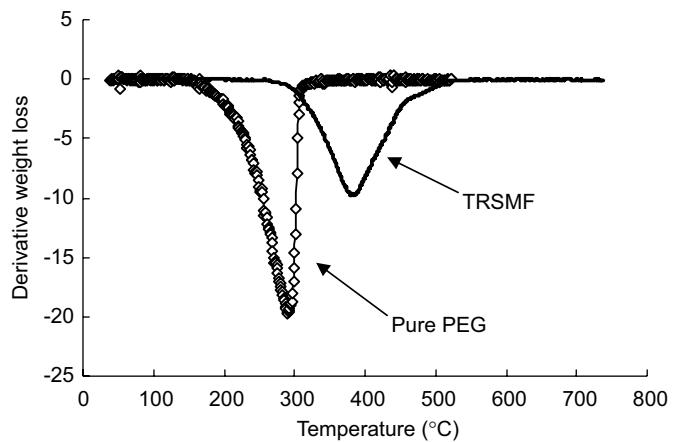
Note:  $T_m$  is the crystal melting temperature,  $T_c$  the crystal crystallizing temperature, and  $\Delta H$  the fusion and crystallizing heat. The PEG crystallinity is calculated from the enthalpy data,  $\Delta H$ , of the crystallization by using the enthalpy value 197 J/g for the fusion of 100% crystalline PEG given by Refs. [59,60].

**Fig. 8.** Log  $E'$ –temperature curve and  $\tan(\delta)$ –temperature curve of TRSMF.

and derivative of thermogravimetry curves of pure PEG and TRSMF are shown in Figs. 9 and 10, respectively. The detailed characteristic temperatures are tabulated in Table 2. The  $T_{10\%}$  of TRSMF is 320.1 °C and  $T_{50\%}$  is 372.6 °C, while those of pure PEG are 221.6 and 272.4 °C, respectively. The peak decomposition point of TRSMF and pure PEG obtained from derivative of thermogravimetry is 383.2 and 290.2 °C, respectively. These suggest that the TRSMF as a PCM has higher heat-resistant performance and as a result it will have a broader applicable temperature range compared to pure PEG.

### 3.7. Thermo-mechanical cyclic tensile testing

The cyclic strain–stress curves of PEGPU obtained by thermo-mechanical cyclic tensile are shown in Fig. 11. The significant

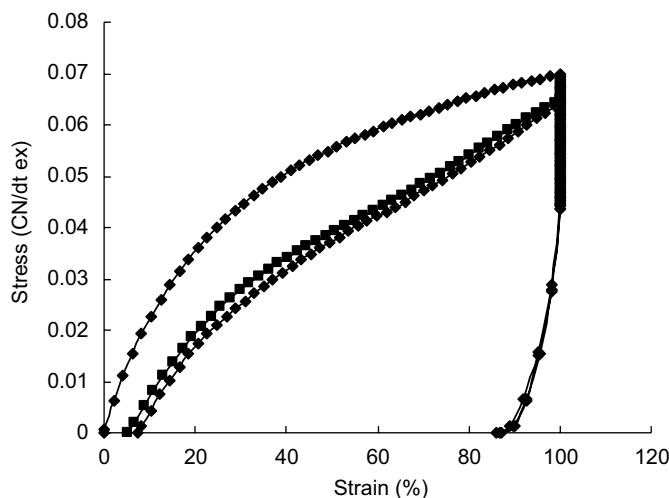
**Fig. 9.** Thermogravimetry of pure PEG and PEGPU.**Fig. 10.** Derivative of thermogravimetry of pure PEG and PEGPU.**Table 2**  
Characteristics temperatures of pure PEG and TRSMF in air

Sample	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{max}$ (°C)
PEG	221.6	272.4	290.2
TRSMF	320.1	372.6	383.2

$T_{10\%}$ : temperature at 10 wt% decomposition;  $T_{50\%}$ : temperature at 50 wt% decomposition;  $T_{max}$ : the maximum decomposition temperature.

difference between the first thermal cycle and the remaining cycles is because of the reorganization of polyurethane molecules involving molecule orientation, crystallization, and breaking of weak points during elongation. After the first cycle, the thermo-mechanical properties become very similar. This suggests that TRSMF has good thermo-mechanical cyclic properties. Detailed shape fixity ratios and recovery ratios are tabulated in Table 3. TRSMF has a fixity ratio of more than 85.8% and a recovery ratio more than 95.4%. At 60 °C, the maximum stress is more than 0.06 cN/dtex at 100% elongation.

The TRSMF shape memory effect accompanied with phase change effect can be illustrated as follows. In the unstretched state, the PEG phase in the TRSMF has high crystallinity, as shown by differential scanning calorimetry. The hard segments form a hard segment phase through strong hydrogen bonding, which has been testified by dynamic mechanical analysis results. When TRSMF is heated from room temperature to 60 °C, which is above the PEG phase melting transition temperature  $T_{trans}$ , the fiber



**Fig. 11.** Cyclic tensile testing curves of TRSMF.

**Table 3**  
Detailed shape fixity ratios and recovery ratios of TRSMF

Circle no.	$\varepsilon_p(N)$ (%)	$\varepsilon_u(R_f(N))$ (%)	Stress at 100% strain (cN/dtex)	$R_{f\text{tot}}(N)$ (%)	$R_f(N)$ (%)
1	0.0	85.8	0.070	100.00	
2	4.6	86.7	0.065	95.40	95.4
3	6.6	87.2	0.064	93.40	97.9

absorbs heat energy, and as a result the PEG phase melts and becomes a random state. However, the fiber does not break because the hard segment ‘physical cross-links’ restrict the free movement of soft segment phase. When it is stretched, the soft segments are extended. If the temperature is cooled to below  $T_{\text{trans}}$ , the latent heat is released and consequently the soft segments crystallize. As a result, the internal stress is stored in the material and the associated deformation is fixed temporally. However, if it is reheated to above  $T_{\text{trans}}$ , the soft segments absorb heat energy and become flexible and the fiber resumes its original length as a result of the releasing of internal stress stored among hard segments. Therefore TRSMF shows latent heat-storage properties and shape memory effect together.

#### 4. Conclusion

A PEG-based linear chain thermoplastic shape memory polyurethane was synthesized via bulk polymerization. The corresponding fiber, as a temperature-regulating fiber, was fabricated via melt spinning. The fiber’s phase change behaviors, crystalline morphology, dynamic mechanical properties, and temperature-resistant performance were investigated using polarizing optical microscopy, differential scanning calorimetry, dynamic mechanical analysis, and thermogravimetry. The prepared 100-dtex fiber had a tenacity of 0.7 cN/dtex and breaking elongation of about 488%. The PEG soft segment phase transfer of TRSMF between crystalline and amorphous states resulted in heat storage and release. At temperatures above the PEG phase melting transition, TRSMF was still solid because the hydrogen-bonded hard segments restricted the free movement of soft segments. The differential scanning calorimetry results indicated that PEGPU had large latent heat storage of about 100J/g. The crystallizing temperature was 20.9 °C and the melting temperature was 44.7 °C. The dynamic mechanical analysis results showed that it

has a plateau elastic modulus in the region above the PEG phase melting transition while below 160 °C. The thermogravimetry results showed that PEGPU had a much broader applicable temperature range compared to pure PEG. Finally, the thermo-mechanical cyclic tensile testing results suggested that the material has good shape memory effect with a shape fixity ratio of more than 85.8% and a recovery ratio of above 95.4%.

#### Acknowledgment

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