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

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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:

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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, & Martinez, 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).

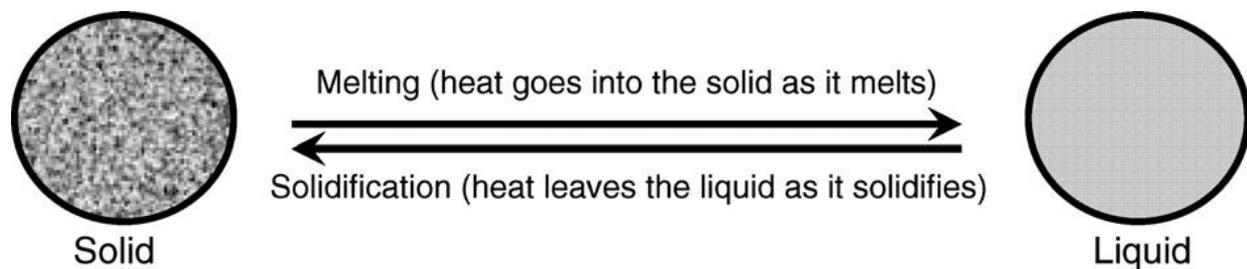


Fig. 2.1. Schematic representation of phase change process

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)

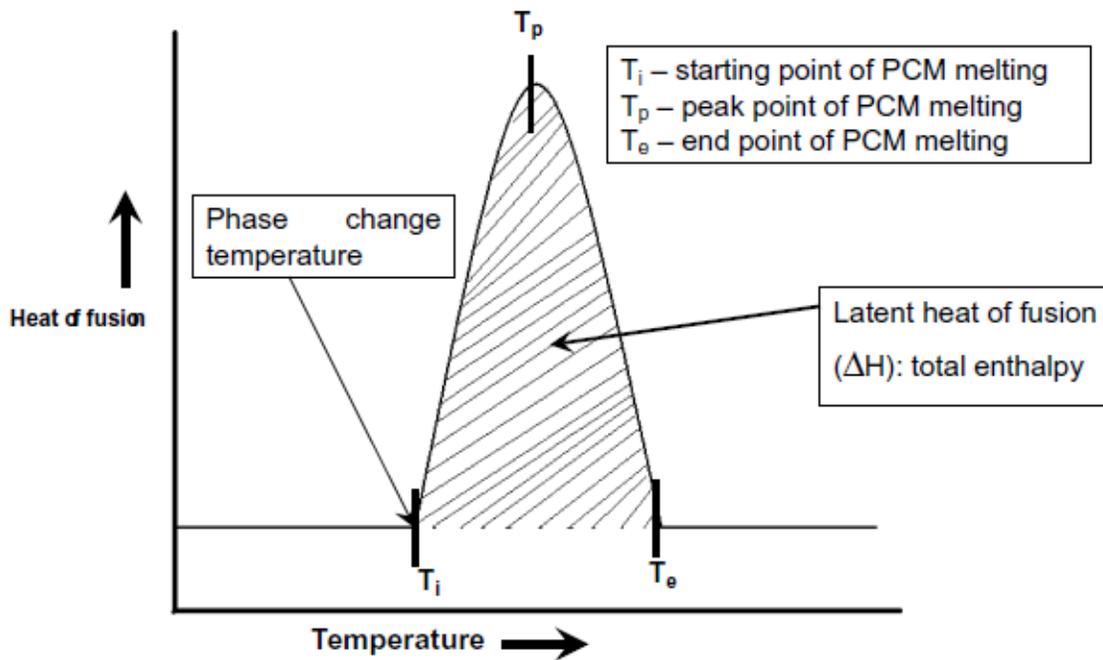


Fig. 2.2. Schematic DSC heating thermo-gram of PCM

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, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{C}_n\text{H}_{2n+2}$. 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 $n = 13\text{--}18$ 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/m³) and a wide range of melting temperatures. The repeating unit of PEG is oxyethylene ($-\text{O}-\text{CH}_2-\text{CH}_2-$)_n, 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, Graber, & 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 an 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.

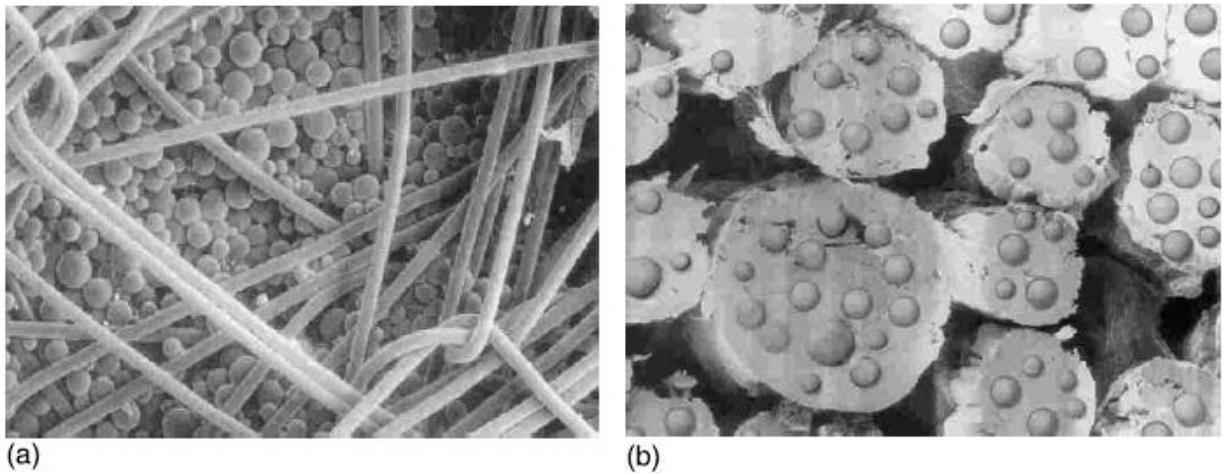


Fig. 2.4. SEM photographs of microcapsules

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 20⁰C and 68⁰C 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 by Younsook, Dong, and Kyunghee, it was seen that Polyurea microcapsules manufactured by interfacial polymerization were melted at curing temperatures higher than 80⁰C (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 10-50⁰C, and the release property by measuring crystallization temperature (T_c) and heat of crystallization (H_c) at 50 to -10⁰C. The heating and cooling rates of the DSC run were both 10⁰C/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, Graber, & 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.

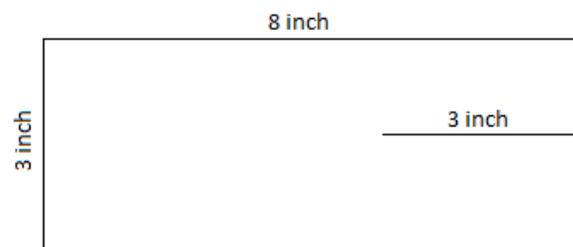


Fig. 3.1. Specimen dimension for tear strength testing

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 Rebp. 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 Rebp 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 Rebp 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 hydroxymethylated 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 monomethylolurea, dimethylolurea, and trimethylolurea.

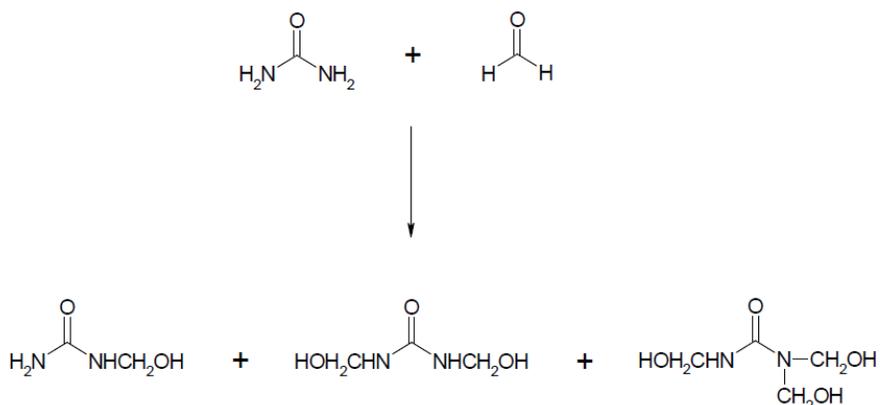


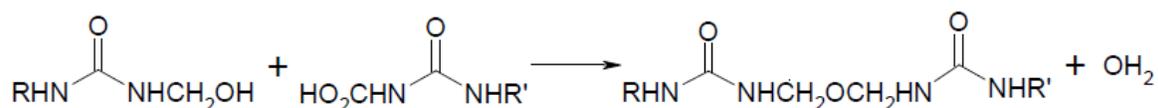
Fig. 4.1. Formation of mono-, di- and trimethylolurea by the addition of formaldehyde to urea

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).

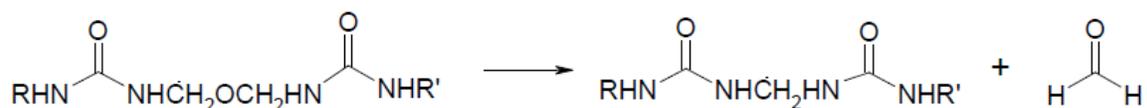
(a)



(b)



(c)



(d)

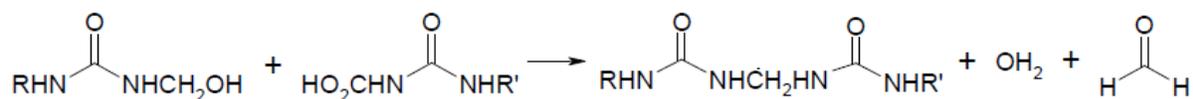


Fig.4.2. Second stage reactions of the urea formaldehyde polymerization, forming higher molecular weight oligomers and polymers

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.

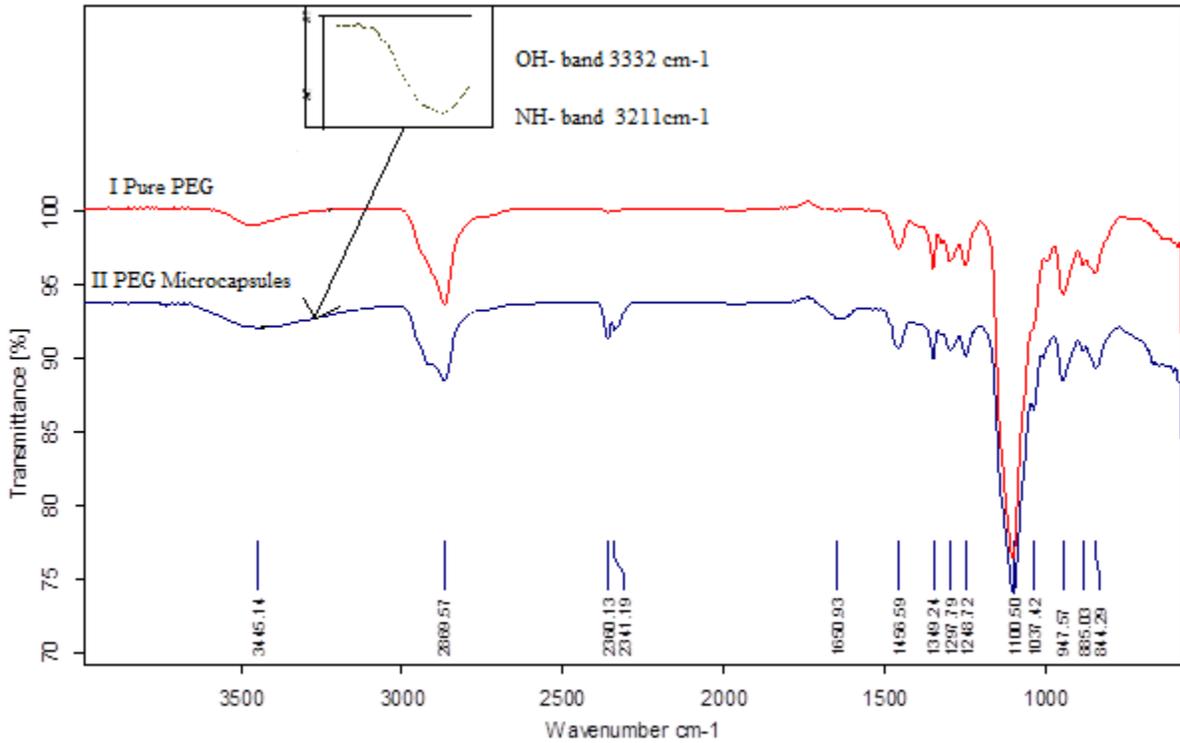


Fig. 4.3. FTIR spectrogram of pure PEG (I) and encapsulated PEG microcapsules (II)

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

The spectrum of the urea-formaldehyde PEG microcapsules shows a strong absorption band at 3332 cm^{-1} . This band is broad and typical of hydrogen bonded N-H and OH. One strong absorption is observed at 1650 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 $3360\text{ -}3390\text{ cm}^{-1}$ 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 CH_2 stretching vibrations near 2800 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

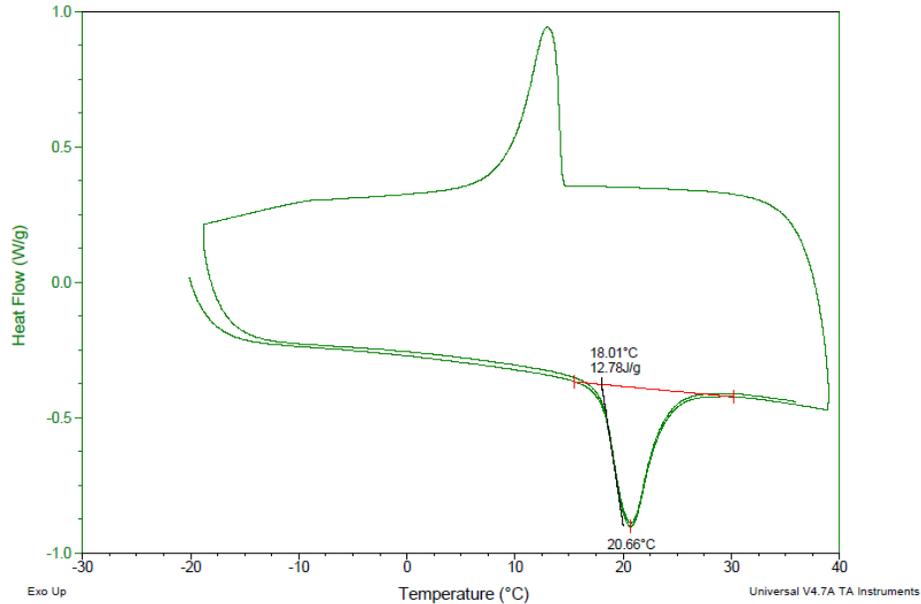


Fig. 4.4. Thermo graph of microcapsules from DSC analysis

The heat cool heat analysis was done of the microcapsules to examine the thermal behavior of PEG. The samples were cooled down at -20°C and then heated up to 40°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°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 12.78J/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°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.

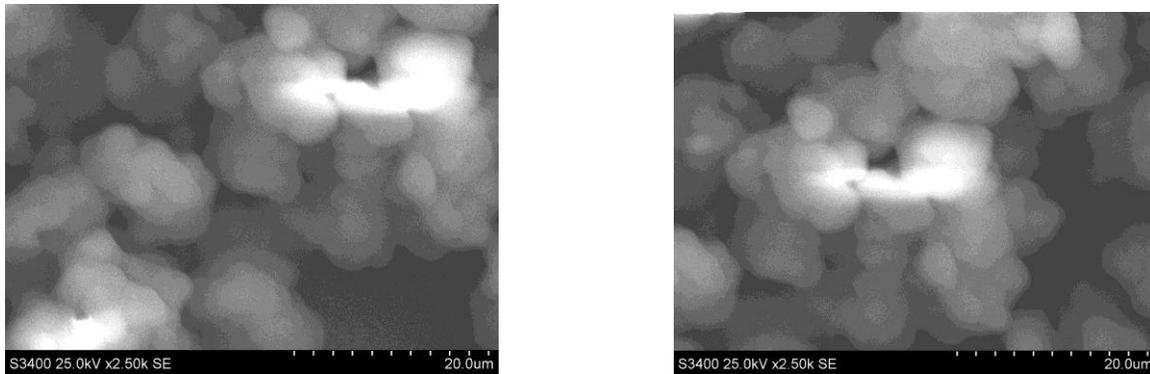


Fig. 4.5. SEM pictures showing the uniform and circular diameter

The average diameter of the developed microcapsules was calculated to be around 30 μm . This indicates that the microcapsules are tiny and easy to coat onto the fabric surface.

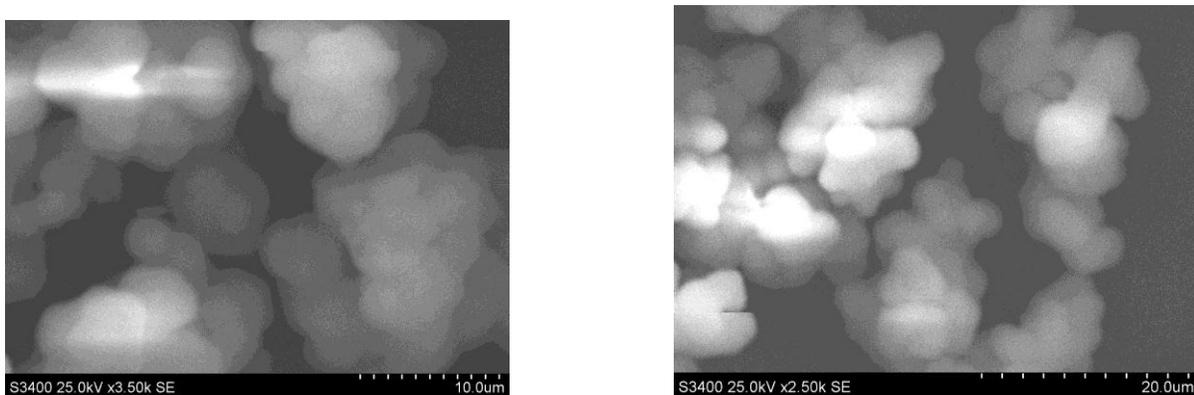


Fig. 4.6. SEM pictures showing the round, spherical, and smooth morphology of the microcapsules

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 folating 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				

Form 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 \overline{M}_w 600, PEG \overline{M}_w 1000, and PEG \overline{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 \overline{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 \overline{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.

REFERENCES

- Brown, E., Kessler, M., Sottos, N., & White, S. (2003). In situ poly (urea-formaldehyde) microencapsulation of dicyclopentadiene. *Journal of Microencapsulation*, 20(6), 719-730.
- Choi, K., Cho, G., Kim, P., & Cho, C. (2004). Thermal storage/release and mechanical properties of phase change materials on polyester fabric. *Textile Research Journal*, 74(4), 292-296.
- Corberán, J, Verde, m, Gil, m, & Martinez, n. (2010). Study of adsorption materials for their application as perspiration-absorbing textiles. *Textile Research Journal*, 80(12), 1160–1171.
- Dubey, R, Shami, T, & Rao, K. (2009). Microencapsulation technology and applications. *Defence Science Journal*, 59(1), 82-95.
- Fan, J, & Cheng, X. (2005). Heat and moisture transfer with sorption and phase change through clothing assemblies. *Textile Research Journal*, 75(3), 187-196.
- Fan, J., & Wen, X. (2002). Modeling heat and moisture transfer through fibrous insulation with phase change and mobile condensates. *International Journal of Heat and Mass Transfer*, 45, 4045–4055.
- Farid, M., Khudhair, A., Razack, S., & Al-Hallaj, S. (2004). A review on phase change energy storage: materials and applications. *Energy Conversion and Management*, 45, 1597–1615.
- Ghali, K, Ghaddar, N, Harathani, J, & JONES, B. (2004). Experimental and numerical investigation of the effect of phase change materials on clothing during periodic ventilation. *Textile Research Journal*, 74(3), 205-214.

Giraud, S. (2005). Flame retarded polyurea with microencapsulated ammonium phosphate for textile coating. *Polymer Degradation and Stability*, 88, 106-113.

Han, S., Kim, C., & Kwon, D. (1997). Thermal/oxidative degradation and stabilization of polyethylene glycol. *Polymer*, 38(2), 317-323.

Horrocks, A. R., & Anand, S. C. (2000). *Handbook of technical textiles*. Cambridge England: Woodhead publishing limited.

Jiang, Y., Ding, E., & LI, G. (2002). Study of transition characteristics of peg/cda solid-solid phase change material. *Polymer*, 43, 117-122.

Jun, Y., Park, C., Shim, H., & Kang, T. (2009). Thermal comfort properties of wearing caps from various textiles. *Textile Research Journal*, 79(2), 179-189.

Khudhair, A., & Farid, M. (2004). A review on energy conservation in building applications with thermal storage by latent heat using phase change materials. *Energy Conversion and Management*, 45, 263–275.

Nelson, G. (2002). Application of microencapsulation in textiles. *International Journal of Pharmaceutics*, 242, 55-62.

O'Mahony, M., & Braddock, S. (2002). *Sportstech : revolutionary fabrics, fashion and design*. London: Thames & Hudson.

Polu, A., & Kumar, R. (2011). Impedance spectroscopy and ftir studies of peg - based polymer electrolytes. *E-Journal of Chemistry*, 8(1), 347-353.

Poly(ethylene glycol). (n.d.). Retrieved from <http://www.chemblink.com/products/25322-68-3.htm>

Rochmadi, A., Prasetya, A., & Hasokowati, W. (2010). Mechanism of microencapsulation with urea-formaldehyde polymer. *American Journal of Applied Sciences*, 7(6), 739-745.

Salaün, F., Bourbigot, S., & Rumeau, P. (2010). Development of phase change materials in clothing part i: formulation of microencapsulated phase change. *Textile Research Journal*, 80(3), 195-205.

Sánchez, P., Sánchez-Fernandez, M., Romero, A., Rodríguez, J., & Sánchez-Silva, L. (2009). Development of thermo-regulating textiles using paraffin wax microcapsules. *Thermochimica Acta*,

Scott, R. (2005). *Textile for protection*. London: Taylor & Francis Inc.

Shim, H., Mccullough, E., & Jones, B. (2001). Using phase change materials in clothing. *Textile Research Journal*, 71(6), 495-502.

Shin, Y., Yoo, D., & Son, K. (2005). Development of thermoregulating textile materials with microencapsulated phase change materials (pcm). iv. performance properties and hand of fabrics treated with pcm microcapsules. *Journal of Applied Polymer Science*, 97, 910-915.

Shin, Y., Yoo, D., & Son, K. (2005). Development of thermoregulating textile materials with microencapsulated phase change materials (pcm). ii. preparation and application of pcm microcapsules. *Journal of Applied Polymer Science*, 96, 2005-2010.

Taboada, M, Graber, T, & Cisternas, L. (2004). Industrial engineering chemistry research. Sodium Carbonate Extractive Crystallization with Poly(ethylene glycol) Equilibrium Data and Conceptual Process Design, 43, 835-838.

Vijayaraaghavan, N., & Gopalakrishnan, D. (2006). Phase change materials for application in textiles. Synthetic Fibers, 11-16.

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 (μm)	Uncoated (μm)
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