DEVELOPMENT OF MULTIFUNCTIONAL TICK REPELLENT TEXTILES

A Thesis

by

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Submitted to the
Graduate School of Science and Engineering
In partial fulfillment of the requirement for
the degree of

Master of Science

In the
Department of Mechanical Engineering

Özyeğin University
September 2016

DEVELOPMENT OF MULTIFUNCTIONAL TICK REPELLENT TEXTILES

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To,

My family, friends and teachers

ABSTRACT

This thesis focuses on smart textile manufacturing with tick repellency through encapsulation of the natural extracts and applying them onto the fabric surfaces. Tick-borne encephalitis (TBE) is a human viral infectious disease involving the central nervous system. TBE cases in Europe have steadily increased over the last few decades. The disease is most often manifested as meningitis (inflammation of the membrane that surrounds the brain and spinal cord), encephalitis (inflammation of the brain), or meningoencephalitis (inflammation of both the brain and meninges). According to the World Health Organization 35-58% of TBE patients suffer long-term neurological problems, such as various cognitive or neuropsychiatric complaints, balance disorders, headache, dysphasia, hearing defects, and spinal paralysis, and 2% die from the disease. Consumer demand for hygienic clothing and active wear has created a substantial market for anti-tick and anti-microbial textile products. Therefore, it is an urgent need to find novel protective methods and/or products that can prevent or minimize the risks of the bites of these deadly insects, and consequently contributing to improvement of human health.

Innovative textile products are continuously being developed and introduced to the market such as the ones with long-lasting fragrances and skin softeners, medical applications such as antibiotics, and antimicrobial agents for medical textiles. These are some applications for which clothing manufacturers utilize resources to add value to textiles in order to increase their competitiveness, improve market dynamics and enable economic growth of the industry. In this thesis work, textiles decorated with nano-micro capsules encapsulating bioactive oils, have been developed and studied for their anti-tick properties to cure and/or prevent the spread of tick-borne diseases.

Encapsulation techniques make use of microcapsules which act as small containers of liquids to be released from the inner core under controlled conditions to address a specific purpose. Empty nano-capsules and capsules with eucalyptus oil as the core ingredient encapsulated by diblock co-polymer: polyethylene glycol-polycaprolactone (PEG-b-PCL) shell, were prepared using solvent evaporation technique. PEG-b-PCL is biodegradable polymer and has been used for its non-toxic nature, ability of maintaining good mechanical integrity until degraded and being capable of controlled rates of degradation. The developed capsules were characterized based on their surface morphology, size, size distribution, surface charge and controlled release. The capsules synthesized in lab along with commercially available polyuria based capsules have been applied to the textile selected, for tick repellency.

In order to systematically study the tick repellency through capsules attachment the textile properties were thoroughly studied initially. For the determination of the best suited textile five different textile samples were studied in the first phase. The textiles studied are (i) %100 carded cotton, (ii) %100 combed cotton, (iii) %100 polyester, (iv) %100 viscose and (v) %100 tencel. Based on the fundamental understanding of the interaction forces it is believed that hydrophobicity should help enhance the attachment of capsules to the textile surfaces due to the hydrophobic-hydrophobic interactions. As a second mechanism, we also concentrated on the electrostatic attraction by tuning the surface charge of the textile and the capsules opposite. Cotton and polyester and their blends were chosen for further study due to their wide availability, use in sports outfits which is also the focus of this project. In addition these fabrics have relatively higher contact angles of 123.38º $\pm$ 3.91º (cotton) and 121º $\pm$ 5.83º (polyester) indicating hydrophobic nature with DI water after treatment in water repelling finishing solution. In the second phase a design of experiment (DoE) was conducted in order to determine

the best textile composition and concentration of silicon in the finishing solution. The DoE revealed 13 tests to be performed for the design of optimum surface properties to enable maximum micro/nano-capsule adherence to the textile samples. The optimization of the responses in DoE was focused on higher hydrophobicity and higher negative surface charge in order to get more amount of positively charged silicon adsorbed. The optimization led to higher desirability for 100% cotton fabric treated with higher silicon content in the finishing solution to maximize the capsules attachment. However, a blend of %65 cotton and %35 polyester was chosen which is suitable for the sports outfits. Yet it has been prepared by weaving cotton fibers on top while polyester fibers on the bottom surface. The idea of this weaving style helps maximize the capsule attachment ability of textile while reducing the need for ironing, which can deform the capsules. The selected textile was treated, sprayed on cotton side, with the prepared nano-micro capsules loaded with eucalyptus oil. The attachment of capsules to the textile was studied by change in the pre and post spray weight of textile. The capsule attachment results from weight difference are in good agreement with predicted capsules attachment obtained from DoE study for a specific combination of textile composition and the concentration of silicon in the finishing solution.

In summary, an optimal textile composition and weaving style was determined in this study to maximize the capsule attachment ability for tick repellency. It was observed that there is a good correlation between the hydrophobic and electrostatic nature of the capsules and the textile surface.

ÖZET

Bu tezin odak noktası, doğal özlerin kapsüllenerek kene kovuculuğu sağlayacak akıllı tekstil üretiminin yapılması ve kumaş yüzeylerinin üzerine uygulanmasıdır. Kene-Kaynaklı Ensefalitin (KKE), merkezi sinir sistemini içine alan, insanlarda bulunan bir viral enfeksiyon hastalığıdır. KKE vakalarının son birkaç yüzyıl içinde Avrupa'da arttığı görülmüştür. Hastalık, çoğunlukla menenjit (beyin ve omuriliği saran zarın iltihaplanması), ensefalit (beyin iltihaplanması) veya meningoensefalit (beyin iltihaplanması ve menenjit) olarak ortaya çıkmaktadır. Dünya Sağlık Örgütüne göre KKE hastalarının %35-58'i, çeşitli zihinsel ve nöropsikiyatrik şikayetler, denge kaybı, baş ağrısı, disfazi, duyma bozuklukları ve omurilik felci gibi uzun dönemli nörolojik problemlerle karşılaşmaktadır ve hastaların %2'si hastalıktan dolayı ölmektedir. Hijyenik kıyafet ve spor giyiminin yüksek müşteri talebi, anti-kene ve anti-mikrobiyal tekstil ürünleri için önemli bir market oluşturmuştur. Bu yüzden, insan sağlığının gelişimini sağlayacak, ölümcül böcek ısırmalarının risklerini minimuma indirecek, özgün koruyucu metotlar ve/veya ürünler üretmek acil bir ihtiyaç haline gelmiştir.

Kalıcı kokular ve cilt yumuşatıcıları, antibiyotikler gibi tıbbi uygulamalar ve tıbbi tekstiller için anti-mikrobiyal ajanlar gibi yenilikçi tekstil ürünleri devamlı üretilmekte ve geliştirilmektedir. Bu gibi uygulamalar, kıyafet üreticileri tarafından, rekabeti arttırmak, market dinamiklerini geliştirmek ve sanayinin ekonomik büyümesini sağlayabilmek için kullanılmaktadır. Bu tez çalışmasında, kene-kaynaklı ensefalitin hastalığının tedavi edilmesini ve/veya yayılmasını engellemesi için, biyoaktif yağların kapsülleme yöntemiyle, nano-mikro kapsüller halinde tekstillere uygulanması üzerine çalışılmış ve geliştirilmiştir. Kapsülleme tekniğinde kapsüller kontrollü koşullarda,

iç dolgusundaki sıvıyı (belirli bir amaca hizmet etmesi için) serbest bırakan küçük konteynerler olarak kullanır.

Boş nano-kapsüller ve taşıyıcı madde olarak okaliptüs yağı içeren kapsüller, diblok kopolimer (polyethylene glycol-polycaprolactone PEG-b- PCL) kullanılarak kapsüllenmiş ve çözücü buharlaştırma yöntemi ile hazırlanmıştır. PEG-b-PCL ayrıştırılabilir bir polimerdir ve toksik olmayan doğası, ayrıştırılana kadar mekanik bütünlüğü sağlayabilme özelliği ve kontrollü oranlarda ayrıştırılabilme özellikleri nedeniyle kullanılmaktadır. Geliştirilmiş kapsüller, yüzey biçimlerine, boyutlarına, boyut dağılımlarına, yüzey gerilimi ve kontrollü salımlarına göre karakterize edilmişlerdir. Laboratuvarda sentezlenmiş kapsüller ve ticari olarak bulunabilen polyüre bazlı kapsüller, kene kovuculuğu test etmek için, seçilmiş tekstiller üzerine uygulanmıştır.

Kapsülleme yöntemiyle kene kovuculuğu sistemik bir şekilde çalışabilmek için, ilk önce tekstillerin temel özellikleri üzerine çalışılmıştır. İlk olarak, en uygun tekstili bulabilmek için, beş farklı tekstil örneği incelenmiştir. Üzerinde çalışılan tekstiller şöyledir; (i) %100 taraklanmış pamuk, (ii) %100 penye, (iii) %100 polyester, (iv) %100 viskoz ve (v) %100 tensil. Temel etkileşim gücü anlayışı doğrultusunda, hidrofobik-hidrofobik etkileşimi sayesinde, hidrofobikliğin, kapsüllerin tekstil üzerine yapışmalarını arttırmaya yardım edeceği düşünülmektedir. İkinci bir mekanizma olarak, tekstilin ve kapsülün yüzey yüklerini zıt hale getirerek, elektrostatik etkileşim üzerine de yoğunlaşılmıştır. İlerleyen çalışmalar için pamuk, polyester ve karışımları, projenin bir odak noktası olan, spor giyimlerindeki yaygın kullanımları dolayısı ile düşünülmüştür. Ayrıca bu kumaşların daha yüksek kontak açıları, $123.38° \pm 3.91°$ (pamuk) ve $121° \pm 5.83°$ (polyester), su itici bitirme solüsyonu içinde işlendikten sonra, kumaşların damıtılmış suya hidrofobik özellik gösterdiğine işaret eder. İkinci aşamada,

en uygun tekstil kompozisyonu ve bitirme solüsyonundaki en uygun silikon miktarını bulabilmek için bir deney tasarımı yürütülmüştür. Deney tasarımı, mikro/nano-kapsüllerin tekstil örneklerine yapışmalarını maksimuma çıkarabilecek optimum yüzey özellikleri için 13 adet test çıkarılmıştır. Deney tasarımının, optimizasyonu için yüksek hidrofibiklik ve yüksek negatif yüzey gerilimi planlanmıştır. Optimizasyon sonucunda, kapsüllerin maksimum yapışmaları için, %100 pamuk kumaşı ve bitirme solüsyonunda yüksek silikon oranı daha optimal bulunmuştur. Buna rağmen, spor giyimi için uygun olan, %65 pamuk ve %35 polyesterin birleşimi tercih edilmiş, yine de kumaş, pamuk ipliklerinin polyester iplikleri üzerine dokunmasıyla hazırlanmıştır. Dokuma, tekstilin kapsüllere tutunma yetilerini arttırırken, kapsüllere zarar verebilecek, ütülenme gereksinimini azaltılmıştır. Seçilen tekstil, hazırlanmış olan, okaliptüs yağı içeren, nano-mikro kapsüllerle pamuklu tarafına spreyle uygulanarak kaplanmıştır. Kapsüllerin tekstile yapışmaları, tekstillerin, spreylemeden önce ve sonraki ağırlıklarına bakılarak analiz edilmiştir. Ağırlık farkıyla ortaya çıkan kapsül tutunma istatistiksel deney analizleri ile belirlenen şartlarla uyumlu bulunmuştur.

Özetle, bu çalışmanın sonucunda, kene kovuculuğu için kapsüllerin tutunmasını maksimuma çıkaracak optimum tekstil kompozisyonu ve dokuma stili belirlenmiş, kapsüllerin ve tekstil yüzeylerinin, hidrofobik ve elektrostatik özelliklerinin kaplama etkenliğine ilişkili olduğu gözlemlenmiştir.

ACKNOWLEDGMENTS

I would first like to thank my thesis advisor Dr. G. Bahar Başım, Associate Professor in the department of mechanical engineering at Özyeğin University Istanbul Turkey. The door to Dr. Başım's office had always been open for me whenever I faced a problem or needed guidance and has consistently steered me in the right direction to accomplish this work.

Besides my advisor I would like to thank Dr. Pınar Özuyar for her help and guidance with the Life Cycle Analysis for TICKOTEX, and Dr. Ayşe Karagöz, for her help with the synthesis of PEG-b-PCL nanocapsules.

My sincere thanks also go to Mr. Gökmen Ukelge (Strategic Planning Manager) at Kivanc Textile Adana Turkey, for providing all the fabrics used in this study.

I would also like to extend my gratitude to TICKOTEX Eureka Project E!8083 for financing this work.

Finally, I must express my very profound gratitude to my family and friends for their unfailing support and encouragement throughout this study. This work would not have been accomplished without you. Thank you!

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Wazir Akbar

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CHAPTER I

INTRODUCTION

1.1. Background

The tick-borne, multi systemic disease, Lyme borreliosis caused by the spirochete Borrelia burgdorferi became a major public health problem in the Central and Eastern European countries. Over the last 30 years, the tick-borne encephalitis (TBE) morbidity increased by 400% (Suss, 2011). Despite extensive research to find treatment for Lyme infection, no cure has been found as of now and up to 35% of the infected people do not respond to treatment or tend to relapse in a short time-frame. In fact, according to the World Health Organization 35-58% of TBE patients suffer long-term neurological problems, including various cognitive or neuropsychiatric complaints, headache, dysphasia, hearing defects, spinal paralysis and balance disorders, while 2% die from the disease (Muller, 2012).

Lyme is caused by the spirochetes that are stealth pathogens and can alter their form or hide within the cells so that the antibiotics cannot affect them (Buhner, 2005). A tick bite may not only cause Borrelia but also co-infections leading to increased cost of Health Insurance System by further complicating the treatment. As an example, in Germany, the expected overall cost for analyses only is estimated to be at 51,215,105C every 2 years (Muller, 2012). People who live and work or go for vacation/recreational activities into potential tick habitats are at obvious risk of acquiring tick-transmitted infections. Therefore, it is an urgent need to find novel protective methods that can

prevent or minimize the risks of the bites of these deadly insects, and consequently contributing to the improvement of public health.

One unique approach to prevent tick borne diseases is to utilize smart textiles. Smart textiles are designed in such a way that upon contact with human body, they are capable of releasing an active substance. One such example is the transfer of skin moisturizing substances in which through the natural movements of the body, the skin is slowly freshened and revitalized for a prolonged period of time by the release of the active agent. To achieve such functional effects, microencapsulation technology seems as an alternative way to provide satisfactory performance with increased durability. Tick repellency can also be achieved using this similar approach.

In view of meeting the customer's increasing demand researchers and textile manufacturers have been investing extensively in smart textiles for research and product development focusing on;

i. The opportunities and limits for cosmetic and health related applications of textiles,
ii. The possible ways of incorporating active substances in a functional manner,
iii. The practical methods of proving the effectiveness of products.

1.1. Literature Review

1.1.1. Functional textiles

Functional textiles are the evolutionary section of the technical textiles market representing an area where textile crosses the conventional boundaries and integrates within the fields of nanotechnology, biotechnology, medicine, etc' to meet the consumers' complex needs and/or requirements. Functional clothing, by definition, is

user-requirement specific and engineered or designed to meet the performance requirements of the user under extreme conditions. A variety of functional clothing products are available in the market as protective clothing, medical clothing or sports clothing etc. Following is the classification of the functional textiles that are under development or already in use.

i. Environmental Hazard Protective
ii. Medical functional
iii. Sportswear
iv. Vanity Clothing
v. Cross-functional Clothing Assemblies
vi. Clothing for Special Needs

The classes listed above provide a clear idea of the distinct applications to which functional clothing cater. New applications and new products continue to appear as this field evolves and grows rapidly on a day-to-day basis (Gupta, 2011).

1.1.1.1. Anti-tick textiles

This thesis focuses on the development of tick repellent textiles i.e. medically functional textiles. There have been many attempts to manufacture insect repellent clothes, mainly dedicated to mosquito and less to other insects such as Ixodes ticks. Most of the repellent clothing contain synthetic insect-repelling agents such as Permethrin (BUZZ OFF Insect Shield™, created by ExOfficio), DEET (N,N-diethyl toluamide), picaridin (a.k.a. Bayrepel) or natural remedies such as essential oils from garlic, citronella, peppermint, geranium, lavender, thyme, lemongrass, cedar, and extracts of pennyroyal, eucalyptus and catnip. However there are many problems

associated with the use of these compounds as repellents for fabrics which can be listed as follows;

i. High toxicity: the synthetic compounds such as DEET, identified as a neurotoxin, being absorbed by skin and causing serious side effects such as dizziness, skin irritation and even death. DEET has an unpleasant odor, attacks plastic materials, low efficiency against ticks and mites.

ii. Low efficiency and high dependency on the repellent concentration existing on clothing and the number of biting insects present: even Bayrepel is more efficient than DEET, however, its activity is poor and it protects humans against ticks only for about two hours (Fradin, 2002). The repellant extracts from plants have very limited spectrum, the repellent effect is short (generally less than two hours), the smell is often disagreeable, may have toxic effects on animals and humans (e.g. tea-tree and thymian oil), and have high potencies to provoke skin irritations and allergies. Essential oils easily permeate into the skin and also can carry other ingredients with them causing adverse effects.

The application of insecticides and acaricides to textiles through microencapsulation to combat dust mites and insects been considered as an alternative approach for retaining the repellant effect for a prolonged period of time while keeping the user protected from excessive dosages of hazardous chemicals. The use of alternative insecticidal compounds such as those found in many essential oils and other plant extracts has made the production of long-lasting acaricide bed sheets possible (Yamada, 1997).

Microencapsulated fabrics are among the latest generation of smart textiles. Encapsulation has allowed moisturizers, therapeutic oils, and insecticides to be

incorporated into fabrics. Buzz Off, originally developed for military, is an encapsulation treatment designed to prevent mosquito bites by using microspheres containing permethrin, a plant extract, which is now being used worldwide for cotton fabrics designed for holiday clothing. A medical application of encapsulation of delivery of drug treatments through clothing, involves the delivery of antimicrobial agents to prevent the bugs from causing the hospital super-infection MRSA. The use of microencapsulation in sportswear, underwear and work wear growing very fast especially in Western Europe, Japan and North America, (Nelson, 2002) and is now becoming a common treatment way for fashion clothing.

1.1.2. Microencapsulation

Microencapsulation is a process by which solids i.e. micro/nano particles, liquids i.e. droplets or even gases may be sealed off in microscopic particles by formation of a thin coating of wall material around the substances. The reasons for microencapsulation are countless. Microencapsulation system offers potential advantages over conventional drug delivery systems and also established as unique carrier systems for many pharmaceuticals (Umer, 2011). **Figure 1.1** shows the general structure of a microcapsule, which generally consists of two major components i.e. the active ingredient and the wall shell.

1.1.2.1. Core material

The core material is defined as the specific material to be coated. It can be liquid or solid in nature. The core material is an active ingredient encapsulated for a specific purpose. The composition of the core material can be varied as the liquid core can include dispersed and/or dissolved material. The solid core can be mixture of active components, stabilizers, excipients, diluents and release-rate retardants or accelerators.

The ability to vary the core materials composition provides definite flexibility and utilization of this characteristic often allows effectual design and development of the desired microcapsules properties (Venkatesan, 2009).

1.1.2.2. Wall/Shell material

Shell or wall material surrounds the active ingredients. It is also referred to as external phase, membrane or matrix. The selection of appropriate coating material decides the physical and chemical properties of the resultant microcapsules/microspheres. While selecting a polymer the product requirements i.e. stabilization, reduced volatility, release characteristics, environmental conditions, etc. are taken into consideration. The polymer should be capable of forming a film that is cohesive with the core material. It should be chemically compatible, non-reactive with the core material and provide the desired coating properties such as strength, flexibility, impermeability, optical properties and stability.

Generally hydrophilic and hydrophobic polymers or a combination of both are used for the microencapsulation process. A number of coating materials have been used successfully in the literature with examples including gelatin, polyvinyl alcohol, ethyl cellulose, cellulose acetate phthalate and styrene maleic anhydride (Spenlehauer, 1986) (Sharifi, 1997). The film thickness can be varied considerably depending on the surface area of the material to be coated and other physical characteristics of the system. The microcapsules may be composed of a single particle or clusters of particles. After isolation from the liquid manufacturing vehicle and drying, the material appears as a free flowing powder. The powder is suitable for formulation as compressed tablets, hard gelatin capsules, suspensions, and other dosage forms (Jain, 1997).

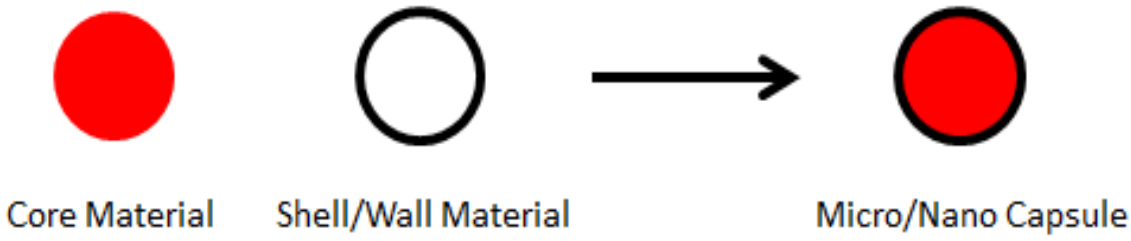


Figure 1.1. The schematic representation of micro-nanocapsule preparation (Chinta, 2013)

The release mechanisms of the core contents vary depending on the selection of wall materials and more importantly, its specific end uses. The core content may be released by friction, pressure, change of temperature, diffusion through the polymer wall, dissolution of the polymer wall coating, biodegradation etc. (Cheng S. Y., 2008).

Historically, the concept of microencapsulation dates back to the 1930s, when Bungenberg de Jong and co-workers were able to entrap microscopic quantities of materials in coacervates. In the early 1950s Barrett K. Green developed the microencapsulation that used the process of phase-separation-coacervation. The first successful commercial development of a product containing microcapsules was "carbonless copy paper" developed by the National Cash Register Company that eliminated the requirement of carbon paper. The first pharmaceutical product consisting of microcapsules was a controlled-release aspirin product. However, the applications of microencapsulation for textile were developed in the 1980s and 1990s, When the US National Aeronautics and Space Administration (NASA) encapsulated phase-change materials (PCMs), space suits for astronauts, with the hope of reducing the impact of extreme variations in temperature in the upper atmosphere. Ultimately the technology was not taken up within the space program. However, the potential was recognized and

after further development the work was licensed by the inventor, the Triangle Research and Development Co. to Outlast Technologies, based in Boulder, Colorado. Outlast has exploited the technology in textile fibers and fabric coatings (Nelson, 2002).

1.1.2.3. The function of encapsulation

The main purpose of microencapsulation is to ensure that the core material reaches the area of interest without getting adversely affected by the environment through which it passes. Therefore, in some cases the core material must be isolated from its surroundings, by the coating material, for example improving the handling properties of sticky materials, or protecting a reactive material from chemical attack etc. In other cases, the main objective is to control the rate at which the core material leaves the microcapsule rather than complete isolation of the core such as in the cases of controlled release of drugs or pesticides etc. Following are the few principal objectives of encapsulation of active materials (Dubey, 2009).

i. Separation of incompatible components
ii. Conversion of liquids into free flowing solids
iii. Increased stability (protection of the encapsulated materials against oxidation or deactivation due to reaction in the environment)
iv. Masking of odor, taste and activity of encapsulated materials
v. Protection of or from the direct environment
vi. Controlled release of active compounds (sustained or delayed release)
vii. Targeted release of encapsulated materials

1.1.3. Techniques for manufacturing of microcapsules

Following are the most commonly used techniques among the many different approaches adopted for preparation of microcapsules.

1.1.3.1. Physical methods

1.1.3.1.1. **Spray-Drying**

Microencapsulation by spray-drying is a low-cost commercial process, which is mostly used for the encapsulation of fragrances and flavors. In spray-drying encapsulation the core material is dispersed in a polymer solution and sprayed into a hot chamber as shown in **Figure 1.2**. In the hot chamber the solvent from the polymer solution evaporates leading to solidification of the polymer onto the core material. The microcapsules prepared with this technique are of polynuclear or matrix type (Ghosh, 2006).

The use of large amounts or the aggregation of core material can lead to lower coating efficiency. However, higher loadings of core particles of up to 50–60% have been reported (Ghosh, 2006). Water-soluble polymers are preferred as shell materials because a solvent-borne system may produce environmental problems and unpleasant odors.

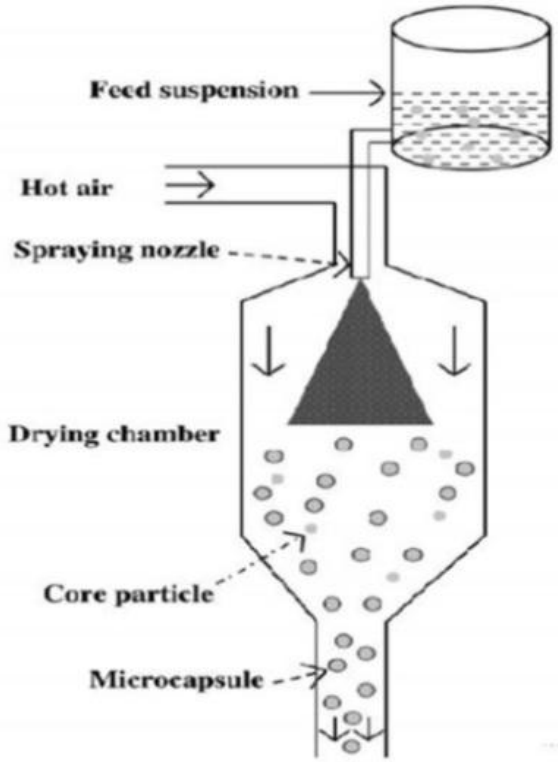


Figure 1.2. Hot chamber used for capsules preparation by spray-drying technique (Chinta, 2013)

1.1.3.1.2. **Air-suspension coating**

The air suspension process offers a wide variety of candidates coating materials for microencapsulation. The process has the capability of applying coatings in the form of solvent solutions, aqueous solution, emulsions, dispersions or hot melt (Bansode et al, 2010).

In this method the particles are coated while suspended in upward-moving air streams. These particles are supported by a perforated plate having different patterns of holes inside and outside a cylindrical insert. Just sufficient amount of air is permitted to rise through the outer circular space to aerate the settling particles. Most of the rising air (usually heated) flows inside the cylinder, causing the particles to rise rapidly. At the top, as the air streams diverge and slow down, the particles settle back onto the outer bed and move downward to repeat the cycle. The particles pass through the inner

cylinder several times in a few minutes cycle. Core materials comprised of micron or submicron particles can be effectively encapsulated by air suspension techniques, but some larger size particles or agglomeration is also, usually, achieved (Bansode et al, 2010).

1.1.3.1.3. **Pan coating**

The pan coating process is extensively used in the pharmaceutical industry and is among the oldest industrial processes for developing small, coated particles or tablets (**Figure 1.3**). The core material is dropped in a pan while the coating material is applied slowly. Solid particles greater than 600 microns in size are generally considered for effective coating by this method.

This process has been widely used for the preparation of controlled-release beads. Medicaments/pharmaceuticals are usually coated onto various spherical substrates such as nonpareil sugar seeds, and then encapsulated with protective layers of various polymers (Bansode et al, 2010).

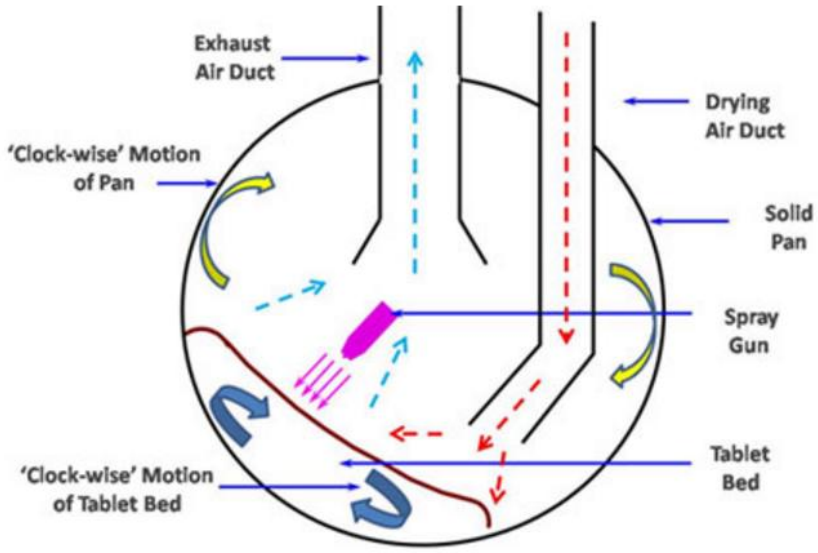


Figure 1.3. Pan coating technique for microcapsules preparation (Colorcon, 1996)

1.1.3.1.4. **Centrifugal Extrusion**

Centrifugal extrusion process is excellent technique for forming, relatively, large diameter capsules of 400-2000μm. This process is only suitable for liquid or slurry because the droplets are formed by the breaking up of a liquid jet. **Figure 1.4** demonstrates a schematic diagram of a centrifugal two-fluid nozzle used to produce microcapsules (Cheng S. Y., 2008).

In centrifugal extrusion processes a rotating extrusion head with concentric nozzles is used coat the wall material onto liquid core materials. The liquid core material is pumped through a central tube while the liquefied wall material is pumped through a surrounding circular tube.

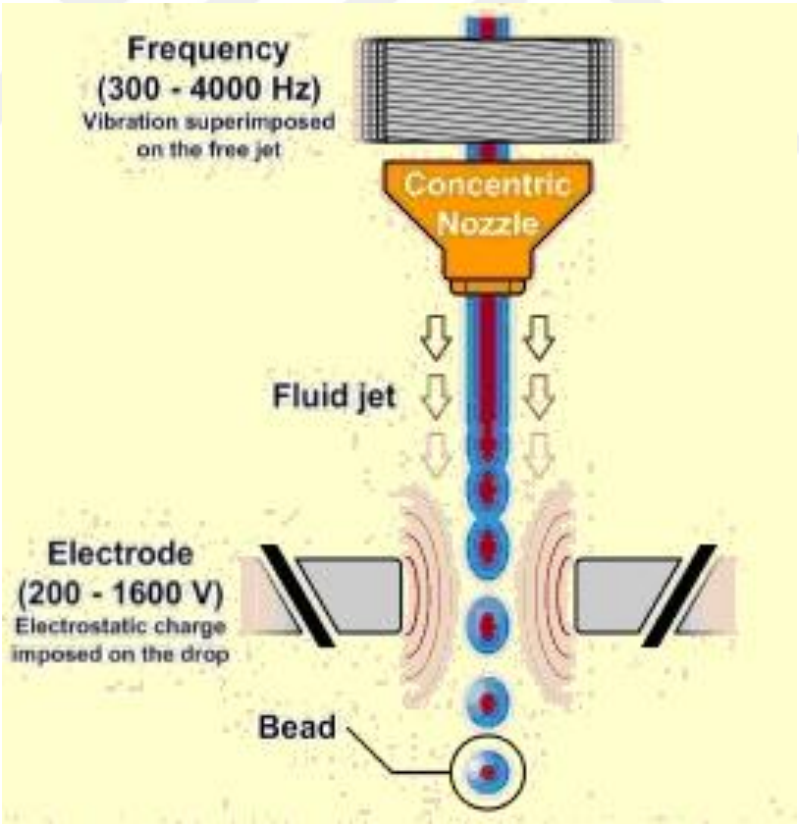


Figure 1.4. Schematic diagram of a centrifugal two-fluid nozzle used to produce microcapsules (Microencapsulation Innovations, 2011)

A layer of wall material is formed around the circular orifice at the end of the nozzle when the core material flows into the layer, which leads to extrusion of a rod like structure of, core and shell, materials. From the rods formed, droplets break away and hardening takes places on a passage through a heat exchanger. In the end solid capsules are removed by filtration or other mechanical means and the immiscible carried fluid is reheated and recycled.

1.1.3.2. Chemical process

1.1.3.2.1. **Solvent Evaporation**

The solvent evaporation process for microcapsule's preparation is carried out in a liquid manufacturing vehicle. The wall/shell material, usually polymer, is dissolved in a volatile solvent. The solvent is immiscible with the liquid manufacturing vehicle phase. A core material to be coated is dispersed in the coating polymer solution. The solution containing core and wall material is the poured drop by drop into the liquid manufacturing vehicle phase i.e. water. During this mixing the liquid manufacturing vehicle is continuously stirred leading to the formation of microcapsules. The solvent is then let to evaporate or mixture is heated (if necessary) so that the solvent for the polymer evaporates.

A matrix-type microcapsule is formed when the core material is dissolved in the coating polymer solution. Once all the solvent for the polymer is evaporated, the liquid vehicle temperature is reduced to ambient temperature with continued agitation. At this stage the microcapsules can be used in suspension form, coated on to substrates or isolated as powders (Dubey, 2009). **Figure 1.5** shows the steps involved in the preparation of microcapsules through solvent evaporation technique (O'Donnell, 1997)

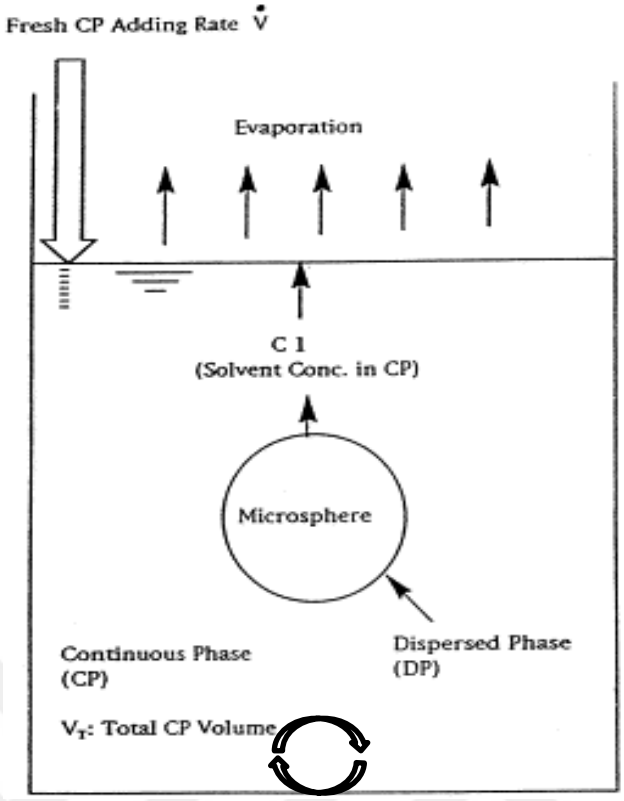


Figure 1.5. Steps involved in solvent evaporation technique for microcapsule preparation (O'Donnell, 1997)

1.1.3.2.2. **Coacervation-Phase separation**

Microencapsulation by coacervation-phase separation process is done in the following three steps under continuous agitation (Kumar et al, 2011).

Step 1: Formation of three immiscible chemical phases**:** In this step three immiscible chemical phases; a liquid manufacturing vehicle phase, a core material phase and a coating material phase, are formed. For the formation of these three phases the core material is dispersed in the solution of the coating material, and the solvent for the polymer is used as the liquid manufacturing vehicle phase.

Step 2: Deposition of coating**:** During this step the liquid polymer coating is deposited on the core material. The deposition of the liquid polymer coating around the

core material occurs if the polymer is absorbed at the interface formed between the core material and the liquid vehicle phase, and this adsorption phenomenon is a prerequisite to the effective coating.

Step 3: Rigidization of coating: This step involves rigidizing the coating, usually by thermal, cross linking, or desolvation techniques to form a self-sustaining microcapsule

1.1.3.3. Polymerization

1.1.3.3.1. **Interfacial polymerization**

Interfacial polymerization, a type of step-growth polymerization, is typically a condensation reaction between two reactants at an interface. The reactants are continuously stirred which causes multiple solutions to be in contact and initiates polymerization at the liquid-liquid interface. The two fast reacting intermediates are dissolved in a pair of immiscible liquids. Most interfacial polymerization reactions utilize Schotten Baumann reaction mechanism, which involves a diacid chloride in the organic phase reacting with a compound containing an active hydrogen atom. Since the two solutions are immiscible so thin flexible walls form rapidly at the interface. Interfacial polymerization can encapsulate both hydrophobic and hydrophilic molecules. Hydrophobic molecules can be encapsulated as long as organic solvents are used and hydrophilic molecules can be encapsulated as long as aqueous solvents are used (Bansode et al, 2010).

1.1.3.3.2. **In-situ polymerization**

The microcapsules produced by this technique range from 3 to 6 um in diameter while the coating thickness ranges 0.2–75μm (0.0079–2.95 mils) (Bansode et al, 2010).

In a few microencapsulation processes, the direct polymerization of a single monomer is carried out on the particle surface. Microcapsule shell formation occurs as a result of polymerization of monomers added to the encapsulation reactor. Polymerization occurs both in the continuous phase and on the interface formed by the dispersed core material and continuous phase and a uniform coating, even over sharp projections, on coated on the core material.

1.1.3.3.3. **Matrix polymer**

A simple method of microcapsules' preparation by matrix polymerization is spray-drying. In spray-drying the particle is formed by evaporation of the solvent from the matrix material however the solidification of the matrix can also be caused by a chemical change. Numerous groups are utilizing polymerization techniques to accomplish microencapsulation. Examples are the National Lead Corporation, Eurand America (Bansode et al, 2010).

Using this phenomenon, Chang prepared microcapsules containing protein solutions by incorporating the protein in the aqueous diamine phase (Bansode et al, 2010). Cheng has demonstrated the permselectivity (the preferential permeation of certain ionic species through ion-exchange membranes), by their ability to convert blood urea to ammonia, the enzyme remaining within the microcapsules when incorporated within an extracorporeal shunt system.

1.1.4. Controlled Release Mechanism of microcapsules

The term Controlled release refers to the management or delivery of compounds as a function of time or in response to stimuli to serve a specific purpose. There are several areas including food science, cosmetics, agriculture, and pharmaceuticals etc.,

where the drug is needed to be provided under particular circumstances. Most commonly it refers to time dependent release in oral dose formulations. The benefit of controlled release is not only prolonged action but it also maintains the drug level within the therapeutic window to avoid potential hazardous peaks in drug concentration and maximize therapeutic efficiency.

Microencapsulation of materials is widely used in many areas to facilitate the capability of reaction, of encapsulated material, to stimuli while protecting the core material from oxidation or adverse effects of the environment it passes through. In addition another advantage of using this technique is the controlled release of the core materials i.e. the core materials will only be released when the desired target is reached.

Generally, the core materials can be released from the capsules by different means such as temperature, pressure and biodegradation etc, (Cheng S. Y., 2009).

The controlled release means that the core materials will not be delivered until the right trigger or environment is encountered. Following are the four most common types of release profiles of microcapsules

i. Trigger release
ii. Sustained release
iii. Burst release
iv. Combination of the above release profiles

The triggered release occurs due to a change in environment such as pH, temperature, moisture, pressure and electromagnetic changes. The objective of the sustained release is achieving the delayed, immediate or pulsatile release profiles. In

burst release case the release will occur after an extended period of time. Following are drug release mechanisms from microspheres.

1.1.4.1. Diffusion

In this release mechanism the active agent is liberated by diffusion through the shell material. It is a time-dependent process in which a random motions of given entities causes the flow of these entities to expand in space. The concept of diffusion driven by a concentration gradient, shell being permeable, allows the core to diffuse out.

1.1.4.2. Dissolution

In dissolution the microcapsules (solid or liquid) are dissolved in a solvent to make a solution. The solvent also dissolves the shell of the capsules, which leads to the release of core material.

1.1.4.3. Molecular Trigger (such as pH)

In this process the pH of the environment works as stimulus that causes the drug release from the shell.

1.1.4.4. Biodegradation

Biodegradation refers to the chemical breakdown of materials by a physiological environment. In some cases the biodegradation of the shell material causes the core material to release from the microcapsules.

1.1.4.5. Thermal Properties

Some shell materials are heat sensitive and capsules made up of those materials release core material when the temperature increases.

1.1.4.6. Mechanical Properties

This is the most common release mechanism that involves friction, which leads to the rupture of the wall so that the core materials can be delivered.

1.1.4.7. Osmotic Properties

In this process the microcapsule absorbs water into the core, which causes the microcapsule to swell and, after enough pressure is built up, the shell of the capsule ruptures and the core is liberated.

1.1.4.8. Biochemical Properties

In this process a chemical reaction causes the shell of the capsule to rupture and releases the encapsulated material.

1.1.5. Applications of Microencapsulation System

Over the last few decades, many new applications of microencapsulation system have been explored in much detail and invented (Nelson, 2002). A few possible uses of microencapsulation techniques in textile industry have been briefly explained below.

1.1.5.1. Phase-Change Materials

Phase-change materials have high heat of fusion and are capable of storing and releasing large amounts of heat. Heat is absorbed or released when the material changes from solid to liquid or vice versa that's why PCMs are classified as latent heat storage (LHS) units.

Microencapsulation technology, with phase change materials (PCM) as core material, was originally utilized in the early 1980s by the US National Aeronautics and

Space Administration (NASA), with the intention of reducing the effect of extreme variations in temperatures, to achieve thermo-regulatory properties of garments particularly in space suits for protecting the astronauts during their missions. The technique was not adopted ultimately in the space program however the potential of this technology was recognized (Nelson, 2002).

A company called Outlast has exploited the technology in textile fibers and fabric coatings and PCM capsules are now applied to in many different areas (Zubkova, 1997) (Colvin, 1998) particularly in outdoor wear (snowsuits, thermals, vests, trousers and parkas etc.) and in the house in blankets, duvets, mattresses and pillowcases. The microcapsules being smaller typically 20–40um in diameter, with a PCM loading of 80–85% provide more surface area for higher heat transfer which makes them react to external temperature rapidly (Pause, 2000). The overall effect of encapsulated PCM attached to textiles can be described as thermoregulation because textiles containing PCMs being designed to combat overheating can also help combat cold.

1.1.5.2. Fragrance Finishes (Aromatherapy)

For many years fragrances have been added to textiles as fabric conditioners to impart fresh aroma to the textile, however the impact is comparatively short lived while through microencapsulation the fragrances can remain on the garment for significant periods of time. Microencapsulation of essential oil flavors has led to many novelty applications, particularly for children's garments and has also allowed exposure to the beneficial effects of aromatherapy both at home and in the work place. Different companies such R T Dodge of Dayton Ohio, Celessence International of Hatch End Middlesex, LJ specialties, UK, Kanebo Gohsen of Osaka Japan, Eldorado International Co, South Korea and a number of other companies have been investigating and

developing microencapsulated fragrances targeting particular applications. For example different plant extracts such as peppermint oil is used in active sportswear, lavender helps people relax, sage and rosemary have been used for odor control in shoe liners and soles and these effects are made last longer through microencapsulation of these essential oils. In the future, for fashion garments, textile industry along with perfume industry may develop garments carrying the smell of branded perfumes, particularly as many perfume firms have already entered into the business of haute couture.

1.1.5.3. Cosmetic Uses

With the rapidly growing trend in enhancing beauty through healthy means, customers' demand for clothing and home textiles having not only their basic characteristics, such as comfort and warmth, but also carrying extra functions as well such as health and beauty care, in an attempt to have a healthier life.

In recent years textiles have also found applications in the cosmetics field i.e. the cosmeto-textiles are the functional garments, which come in direct contact with the skin. These textiles have an encapsulated active ingredient adhered to them. These active ingredients are released for cosmetic purposes to the skin due to friction (rubbing) or heat (generated by human body). Different types of encapsulated materials such as aloe vera, moisturizer and vitamins are applied to cosmeto-garments and are released when needed. The particular purpose of cosmeto-textiles is the promotion of a younger look, i.e. to combat ageing effects. There is also a cosmeto-textile called anti-UV textile which not only prevent the wearer skin from getting tanned, but it also avoids the harmful effects caused by the UV radiation as the reduction in ozone layer in the atmosphere will result in increasing the danger of skin cancer (Cheng S. Y., 2008).

1.1.5.4. Medical/Medicinal Uses

Apart from thermoregulatory and cosmetics applications of microcapsules attached to textiles microencapsulated drugs; medicine are also applied to textiles for medical purposes. As the importance of medical textile has recently been recognized it is under intensive development these days. All the textile materials used for health and hygiene applications come under the umbrella of Medical textiles. Controlled release of drugs can be envisaged for specific forms of medical textiles. The four categories of medical textiles include implantable materials, non-implantable materials, extracorporeal devices, and healthcare's & hygiene products.

Different active agents for wound healing, antimicrobial & antiviral as well as anti-inflammatory agents are encapsulated and applied to textiles to serve their purposes. For example the textiles in contact with wound can release antibiotics, which may lead to decrease in the post-operation infections. The surgical stitches, an example of medical use, release antibiotic around the surgical cut that speeds up the patient recovery and allow the wound to be less frequently redressed. Another application of medical textiles is the use hygiene in the form of surgical gowns containing anti-virus and anti-bacterial agents (encapsulated) which helps in improving the security and protection against liquid-borne pathogens and blood-borne, especially viruses such as human immunodeficiency virus (HIV) which is the primary cause of acquired immune deficiency syndrome (AIDS) and also hepatitis B.

1.1.5.5. Photochromic and Thermochromic Microcapsules

This is an alternative form of color changing technology and generally used in novel applications such as battery testers, stress testers and forehead thermometers. In textiles this technology is finding new application such as product labeling, medical and

security applications as well as there is a continued interest in novelty textiles including swimwear and T-shirts.

Following are two major types of color-changing systems namely

i. Photochromatic: Alters color in response to UV light.
ii. Thermochromatic: Changes the color in response to the temperature.

Both the systems are very sensitive and are protected from the external environment by encapsulation. Heat generated by the contact between textile and human body can make thermochromic systems give us a signal by a change in its color. Melamine-formaldehyde and urea are the most commonly used microencapsulation systems for thermochromic and photochromic inks. New technologies of color changing such as microencapsulated hydrochromic and piezochromic dyes are being developed which in response to water and pressure, respectively, their change color (Aitken, 1996).

1.1.5.6. Flame Retardant Capsule Applications

The microencapsulation provides the flame retardant material with protection (shell) which makes it durable without causing any harm to the person in contact with them, working under severe conditions like firemen. Fire retardants have been applied to many textile products, but in some cases they can reduce the softness, affect the overall handling ability. Microencapsulation has been used to overcome these problems for example in fabrics used in military applications such as tentage (Kover, 1997).

1.1.5.7. Miscellaneous Applications

There are countless applications of microencapsulation technology. It has been used in different areas and considered as most effective mechanism of retaining the

effect for prolonged periods of time while protecting the user from excessive dosages of hazardous chemicals without affecting the durability of the product.

A team of workers in France, working on a variety of fabrics, has encapsulated glycerol stearate and silk protein moisturizers for application on support hosiery and bandages (Dim, 1999). The material maintains skin quality as well as comfort through extensive medical treatment by releasing the active agents where textiles are in direct contact with the skin. A cleaning/wiping cloth with very good cleaning properties containing microencapsulated (in polypropylene nonwoven material) octane, tung oil and paraffin oil as cleaning solvents has been produced by Mitsubishi Paper Mills using (Yokato, 1998). Textiles with different insecticide to combat dust mites and insects have been investigated by many researchers. The use of microencapsulation of alternative insecticidal compounds such as many plant extracts has made possible the development of long-lasting miticidal bed sheets (Yamada, 1997).

1.2. Objective and scope of Study: Development of Anti-Tick Textiles

The main objective of the project is to develop novel multifunctional textile structures that include biological active compounds, to prevent the spreading of infectious diseases like Borreliosis and other tick-borne bacterial diseases. The objective will be achieved in the following three steps;

i. Application of nanotechnology to enhance structure of the textiles to be able to manipulate the adherence of the tick repellent agents.
ii. Develop methodology to enhance coating of tick repellent agents on the textiles.
iii. Organize the toxicity tests to determine the most optimized coating properties.

CHAPTER II

SELECTION OF TEXTILES FOR TICK REPELLENCY

2.1. Introduction

Textiles have long been recognized as being prone to the growth of microorganisms both as a support and food. These microorganisms may exist in the environment even at unfavorable conditions and can quickly grow when the suitable moisture, nutrient and temperature conditions are available. The growth of these microbes on textiles during their use or storage not only degrades the performance of the textile itself but also negatively affects public health. Synthetic fibers, due to their high hydrophobicity, are generally more resistant to attacks by microorganisms than natural fibers (Purwar, 2004). The application of durable antimicrobial finishing to textiles, or incorporating biocides into fibers during extrusion, can control the detrimental effects caused by microbes (Gao, 2008). The attachment of antimicrobial agent to the textile depends upon the surface finish, fabric composition and the weaving style of the fabric.

The effect of weaving pattern and thread density can significantly influence the hydrophobic and hydrophilic performance of the textile surfaces. An increase in thread density often increases surface roughness and interfacial area between the liquid droplet and the textile surface. A study from the International Journal of Clothing Science and Technology found that weaving style affects the physical and mechanical properties of the fabric more than the fiber mix and type in the weft yarn (Mehmet, 2014). Therefore weave pattern and thread count are critical to the design of smart textiles.

This chapter provides a general description of five different 100% single fiber textiles used in the study followed by the principal theories of hydrophobicity and oleophobicity. The selection of the best textiles material for tick repellency is the most important issue to take care of. In general textile hydrophobicity, surface roughness, surface charge etc. should be taken into account when selecting textile.

Polyester and Cotton were selected, after initial study of five different 100% single fiber textiles, for testing because of their wide availability in the textile industry and unique hydrophobic properties. This chapter reports a systematic approach for optimizing the two basic factors that affect the hydrophobic behavior of the textile in order to manipulate the adherence of the microcapsules having bioactive agents encapsulated in them to the textile's surfaces. A design of experiment using response surface central composite model was used to study surface properties of the textile as a function of textile fiber type and the concentration of silicon (hydrophobic component) in the finishing solution for maximum adherence of the nano-microcapsules to the textile surfaces.

2.2. Experimental

2.2.1. Initial study of five different 100% single fiber textiles

In the first phase five different textile samples i.e. 100% Carded Cotton, 100% Combed Cotton, 100% Polyester, 100% Viscose and 100% Tencel. The textile samples were characterized by measuring their Contact angle, surface charge and weaving pattern (microscopy). Based upon their higher hydrophobicity and wide availability 100% carded cotton and 100% Polyester and their blends were chosen for further studies.

2.2.1.1. Contact Angle Measurements

Contact angle was determined by the sessile drop method with "Attension theta light optical goniometer" using one frame per second shutter speed. The experiments were done in triplicate for each sample to measure contact angle of the three-phase interface during the first frame of the droplet formation on the textile surface.

2.2.1.2. Zeta potential Measurements

Zeta potential (ζ) is a scientific term for the electrokinetic potential in colloidal dispersions, which describes the charging behavior at the solid-liquid interface. It is caused by the net electrical charge contained within the region bounded by the slipping plane, and also depends on the location of that plane. It is widely used for quantification of the magnitude of the charge and is determined by the measurement of an electrokinetic effect, which is observed when a solid and a liquid phase move relative to each other.

In this study the zeta potentials, of the different textile samples treated with finishing solution, was studied in order to be able to relate it to the surface charge of the microcapsules, containing bio-active ingredients, which are to be attached to them. Zeta potentials of the textiles were measured by using streaming potential measurement technique with SurPASS by Anton Paar. 1mM KCL solution was used as electrolyte for the analysis of zeta potential in the experiments while 0.05M HCL was used for the pH titration. pH is one of the most important parameters to evaluate the liquid phase that affects the zeta potential and must always be reported with the corresponding zeta potential measurements. **Table 2.1** further lists the factors on both the solid surface and the liquid phase that affect the zeta potential at the solid-liquid interface.

Table 2.1. Factors affecting zeta potential

<table>
<tr><th>Liquid properties</th><th>Solid Properties</th><th>Other</th></tr>
<tr><td>pH value</td><td>Size</td><td>Measuring time</td></tr>
<tr><td>Ionic Strength</td><td>Porosity</td><td>Temperature</td></tr>
<tr><td rowspan="2">Additive concentration</td><td>Electronic conductance</td><td rowspan="2">Material Swelling</td></tr>
<tr><td>Surface roughness</td></tr>
</table>

2.2.1.3. Effect of Weaving

The effect of weaving pattern and thread density can significantly influence the hydrophobic and hydrophilic behaviors of textile. The effect of weaving style of the fibers has been considered in this study to fully understand the hydrophobic response and microcapsule adhesion to the textile surfaces. The micrographic images, of %100 single fiber textile samples, Carded Cotton, Combed Cotton, Polyester (PES), Viscose, and Tencel (TEN), were taken using Carl Zeiss Axio Scope A1 MAT.

2.2.2. Textile Selection Criteria

Hydrophobic properties are desirable on the textiles because they promote a clean textile surface and are also necessary for the adherence of hydrophobic microcapsules. Therefore, hydrophobic behavior and microcapsule adherence in response to textile surface properties has been the main focus for textile selection and design. Microcapsule adherence is dependent on the textile's surface charge, hydrophobic response, mechanical entrapment, and fabric microcapsule absorbance.

Maximum microcapsule adherence is imperative for effective long lasting tick repellent textiles and in this study the capsules adherence through hydrophobic-hydrophobic interaction has been the main criteria for the textile selection.

2.2.2.1. Design of Experiment (DoE)

A design of experiment with two factors revealed 13 tests that must be conducted in order to optimize the textile's hydrophobic properties and microcapsule adherence to them. The experimental design can be seen in **Table 2.3**. This design of experiment investigates change in weight per unit area before and after treating the textile samples with the finishing solution, contact angle determined with DI water and Acacia oil on the textile surface and the surface charge (Zeta Potential) of the textile samples as responses to textile fiber composition and concentration of the silicon in the finishing solution (the two variables).

2.2.2.1.1. **Selected Design Factors**

2.2.2.1.1.1. **Fiber Composition**

Polyester and carded cotton were selected for testing because of their wide availability in the textile industry and unique hydrophobic and hydrophilic properties. The effect of fiber composition on hydrophobic properties has been studied as a function of percentage of polyester fibers in polyester/cotton textile blends having similar weave pattern and thread density.

2.2.2.1.1.2. **Concentration of silicon in finishing solution**

Concentration of silicon in the finishing solution is investigated in order to determine the effect of finishing solution composition on textile hydrophobicity and

microcapsule adherence. The concentration of silicon in the finishing solution is an important factor in textile treatment design and was chosen for studying its effect on the hydrophobic properties of the textile surfaces.

2.2.2.1.2. **Responses**

Following are the responses studied in order to evaluate the behavior of the textile samples treated with different sets of the selected factors, explained above.

2.2.2.1.2.1. **Change in Weight Per Unit Area (g/m^2)**

Different textile samples were treated with different concentration of silicon in the finishing solution. The change in weight per unit area was calculated by the difference in the weight before and after treating the textile samples with the finishing solution.

2.2.2.1.2.2. **Contact Angle Measurements with DI_Water (Degrees)**

Contact angle was determined by sessile drop method using Attension theta light optical goniometer. Three experiments were carried out with one frame per second shutter speed to measure the contact angle, after one second of dropping the water droplet on textile the surface.

2.2.2.1.2.3. **Contact Angle with Essential Oil (Degrees)**

The contact angles of essential oils have been measured in a similar manner as with DI water. Eucalyptus oil and lavender oil were initially used to start the evaluations since they are the two chosen extracts allowed by the EU regulations to be used as the tick repellants, later on the contact angle of acacia oil has also been measured.

2.2.2.1.2.4. **Surface Charge [Zeta Potential (mV)] Measurements on Textiles**

Zeta potential values of the textile blends treated with different concentrations of silicon in the finishing solution were measured using the same method described in section 2.2.1.2. The values of zeta potential were extrapolated for pH lower than 3.5 of the circulating electrolyte.

2.2.2.1.2.5. **Isoelectric Point (IEP) Determination of Textiles**

When reporting zeta potential data, it is very important to refer to the pH of the aqueous solution used for the zeta potential analysis. A primary purpose of a pH titration of the solid-liquid interface is the assessment of the isoelectric point (IEP). At a certain pH the zeta potential of the surface reaches 0 V and reverses its sign when moving from high to low pH and vice versa. The pH of the aqueous solution at which the zeta potential reverses its sign is known as the IEP. Hence, the surface charge is pH dependent and it must always be reported with the corresponding zeta potential. The isoelectric points of the textile's blends were determined by extrapolation for pH lower than 3.5 of the circulating electrolyte.

2.2.2.1.3. **Optimization**

For all the responses, obtained, during the design optimization process, ratios of their maximum to minimum value were within the range suggested by the Design Expert Software and a linear model fit was used for all of the selected responses.

In the optimization process, contact angles with DI water and zeta potential at the pH of DI water are taken as the most important responses in order meet the need for maximum capsules attachment. Therefore the desirability for the contact angle with DI

water was set to maximum while for the zeta potential at the pH of DI water was set to least negative. The reason behind this is that it would result in most amount of positively charged silicon adsorption onto the textile surfaces. Silicon is the hydrophobic component of the finishing solution. Higher adsorption of silicon on textile surfaces would lead to higher hydrophobicity and the less negative zeta potential (by neutralizing the surface charge of negatively charged textile surfaces) of the treated textile samples. These two factors i.e. higher hydrophobicity and the less negative zeta potential would result in higher capsule attachment to textile surfaces through hydrophobic-hydrophobic interaction. This idea is based on the assumption that the capsules being developed will be hydrophobic due to their hydrophobic polymeric content.

2.3. Results and Discussion

2.3.1. Initial study of five different 100% single fiber textiles

2.3.1.1. Contact Angle Measurements

Eucalyptus and lavender oil were observed to have no measurable contact angles on the textile surfaces. **Table 2.2** displays the weight per unit area and contact angles of distilled water (DIW) and Acacia oil before and after treatments with finishing solution for %100 single fiber compositions of carded cotton, combed cotton, polyester, viscose, and tencel textile samples. Reported contact angles represent the average of three measured contact angles on sample surface along with standard deviation.

Table 2.2. Contact angles of different %100 single fiber compositions. Standard deviations are represented as a ± uncertainty

Fiber Type	*Weight (g/cm2)*	*Contact Angle before treatment (Degree)*		*Contact Angle after treatment (Degree)*	
		DIW	*Acacia Oil*	*DIW*	*Acacia Oil*
%100 Carded cotton	0.0284	109.3±5.8	112.23±1.4	111.49±7.3	121±5.8
%100 Combed cotton	0.0273	0	88.12±8.1	117.84±5	110.75±3.8
%100 PES	0.0135	84.28±6.7	59.38±12	106.86±2.4	123.38±3.9
%100 Viscose	0.0156	0	23.36±9.5	0	115±5
%100 Tencel	0.0205	0	76.48±2.99	101.64±5.5	120.9±3.21

2.3.1.2. Zeta potential

Zeta potentials for %100 single fiber compositions of Carded Cotton, Combed Cotton, Polyester, Viscon and Tencel, treated with finishing solution, as a function of pH are shown below in **Figure 2.1.** The isoelectric points of the fabrics can be found at the intersection of the zero potential line. The fabrics, %100 polyester and %100 cotton were found to have lower (more negative) zeta potential as compared to the others. The %100 Tencel fiber composition exhibits the highest pH at its isoelectric point and %100 Combed Cotton has the lowest pH at its isoelectric point.

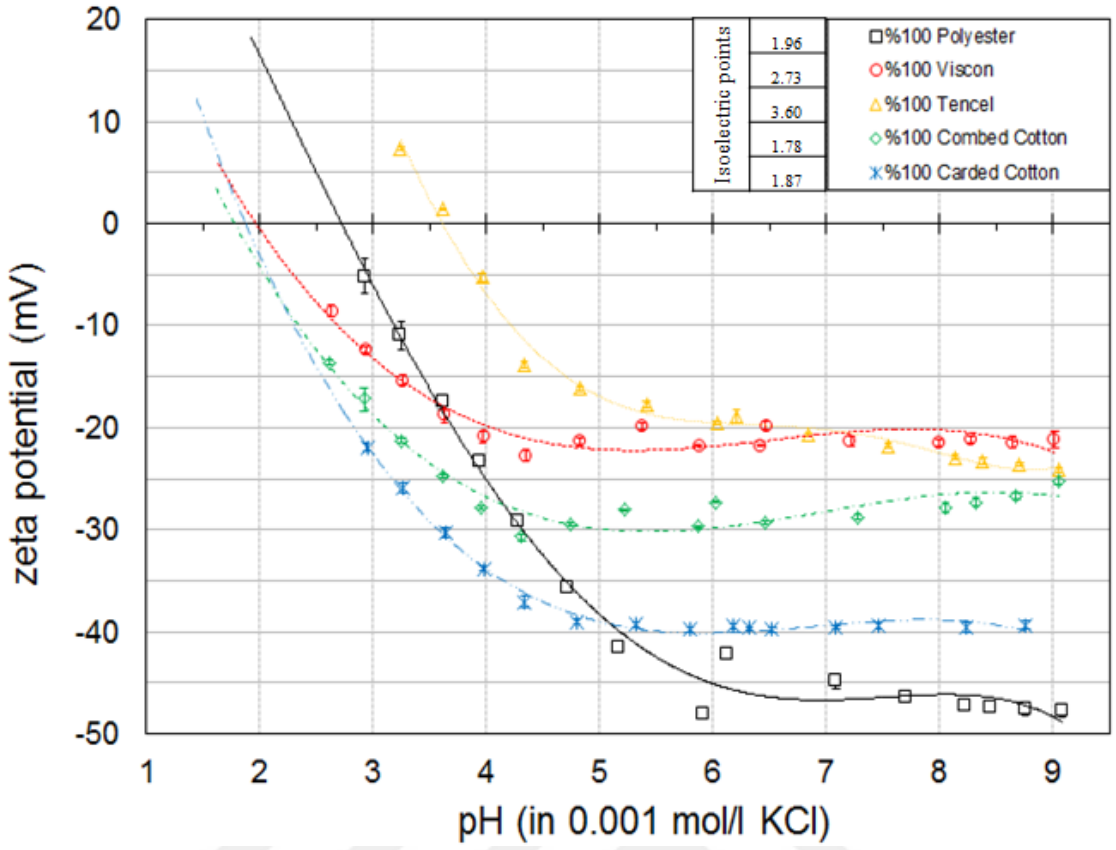


Figure 2.1. Zeta potential of different textile samples as a function of pH

2.3.1.3. Effect of Weaving

Data from **Table 2.2** shows that the average contact angle for untreated and treated %100 Combed cotton is 0° and 118° respectively, and the contact angle for untreated and treated Carded Cotton is 109° and 111° respectively. The two fabrics have the same %100 Cotton fiber composition, but differ in thread weaving pattern. The change in weave pattern has resulted in a difference in their wettability. The **Figure 2.2** in the following shows the micrographs of 100% single fiber textiles at different magnifications. It can clearly be seen that there is a difference in the thread density and weaving pattern.

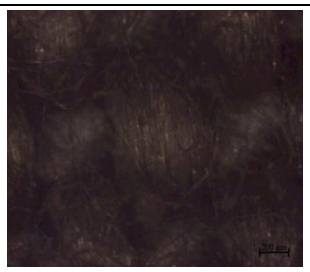
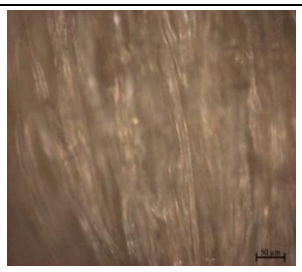
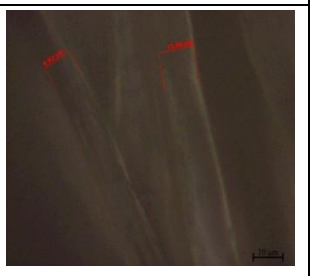
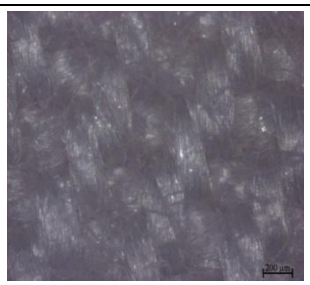
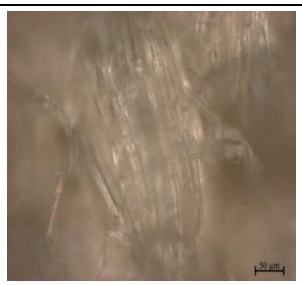
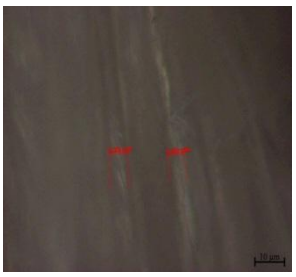
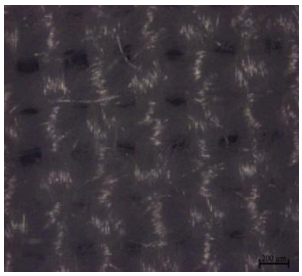
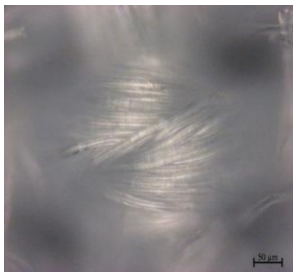
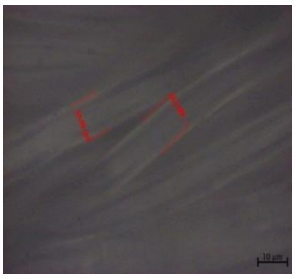
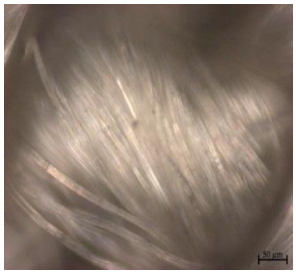
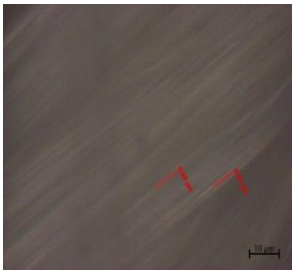
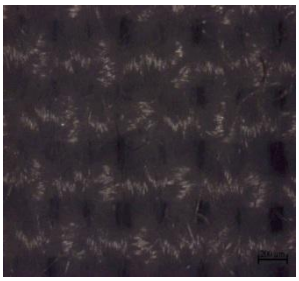
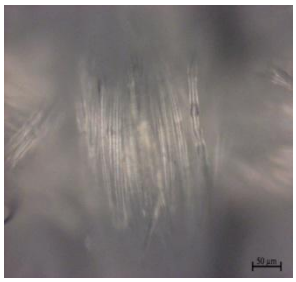
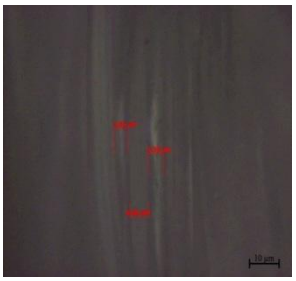
Composition (%100)	*Magnification*		
	200 um	*50 um*	*10 um*
Carded Cotton			
Combed Cotton			
Polyester			
Viscose			
Tencel			

Figure 2.2. Micrographs of %100 single fiber textiles at different magnification

2.3.2. Textile Selection Criteria

Hydrophobic properties promote a clean textile surface and are necessary for the adherence of hydrophobic microcapsules and therefore have been the main focus of the study for textile selection and design. Moreover, the attachment of microcapsule is dependent on textile surface charge, hydrophobic response, mechanical entrapment, and fabric microcapsule absorbance. Based upon the initial study, cotton, polyester and their blends were selected for further investigation because of their unique hydrophobic properties, wide availability and already in use in sportswear. In the second phase of textile selection a design of experiment has been carried out to determine the optimum silicon concentration in the finishing solution and the fiber composition to maximize the hydrophobic properties and microcapsule adherence to textile surfaces.

2.3.2.1. Design of Experiment (DoE)

A design of experiment using response surface central composite model was used to study the surface properties of the textile as a function of the following two factors.

i. Fabric composition (%polyester content)
ii. Concentration of silicon in the finishing solution

The DoE revealed 13 tests to be carried out in order to have optimized hydrophobic properties and microcapsule adherence to textile's surfaces. The experimental design can be seen in **Table 2.3**.

Table 2.3. Experimental design suggested by the 2 variable DoE.

Std	*Run*	*Type*	*Fiber Composition (% PES)*	*Finishing Solution (Silicon Conc.)*
1	1	Block 1	20	6
2	2	Block 1	80	6
3	3	Block 1	20	24
4	4	Block 1	80	24
5	5	Block 1	0	15
6	6	Block 1	100	15
7	7	Block 1	50	0
8	8	Block 1	50	30
9	9	Block 1	50	15
10	10	Block 1	50	15
11	11	Block 1	50	15
12	12	Block 1	50	15
13	13	Block 1	50	15

2.3.2.1.1. **Responses**

The effects of the fabric composition and concentration of silicon in the finishing solution on the following responses have been studied in order to evaluate the behavior of the textile samples.

2.3.2.1.1.1. **Change in Weight Per Unit Area (g/m^2)**

The change in weight per unit area of the textiles as a function of the fiber composition and finishing solution (with changing concentration of silicon) is given in **Figure 2.3**. It can be seen that the surface plot in **Figure 2.3** is a flat horizontal surface which indicates that there no significant change in the areal densities of the textiles before and after treatment with finishing solution.

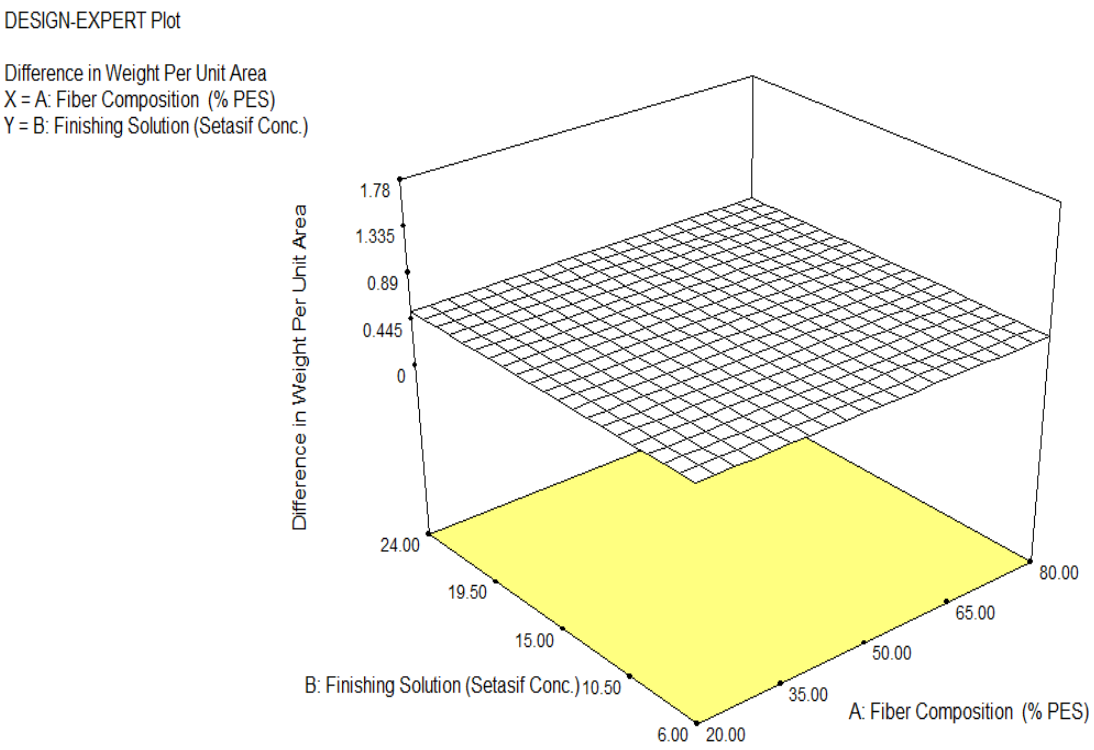


Figure 2.3. Change in weight per unit area of the textiles vs. fiber composition and finishing solution (with changing concentration of silicon)

2.3.2.1.1.2. **Contact Angle with DI_Water (Degrees)**

Figure 2.4 illustrates the contact angle obtained by a DI water droplet on the textiles with varying fiber composition and treated with different concentration of silicon in the finishing solution. The reported contact angles represent the average of three measured contact angles on the sample's surface. From **Figure 2.4** it can be seen that the contact angle measured on the textiles increases with the increasing concentration of silicon in the finishing solution and decreasing polyester fiber content in the fabric. These results suggest that higher cotton content fabric treated with higher silicon concentration in the finishing solution should retain more of the hydrophobic capsules due to increased hydrophobic-hydrophobic interactions.

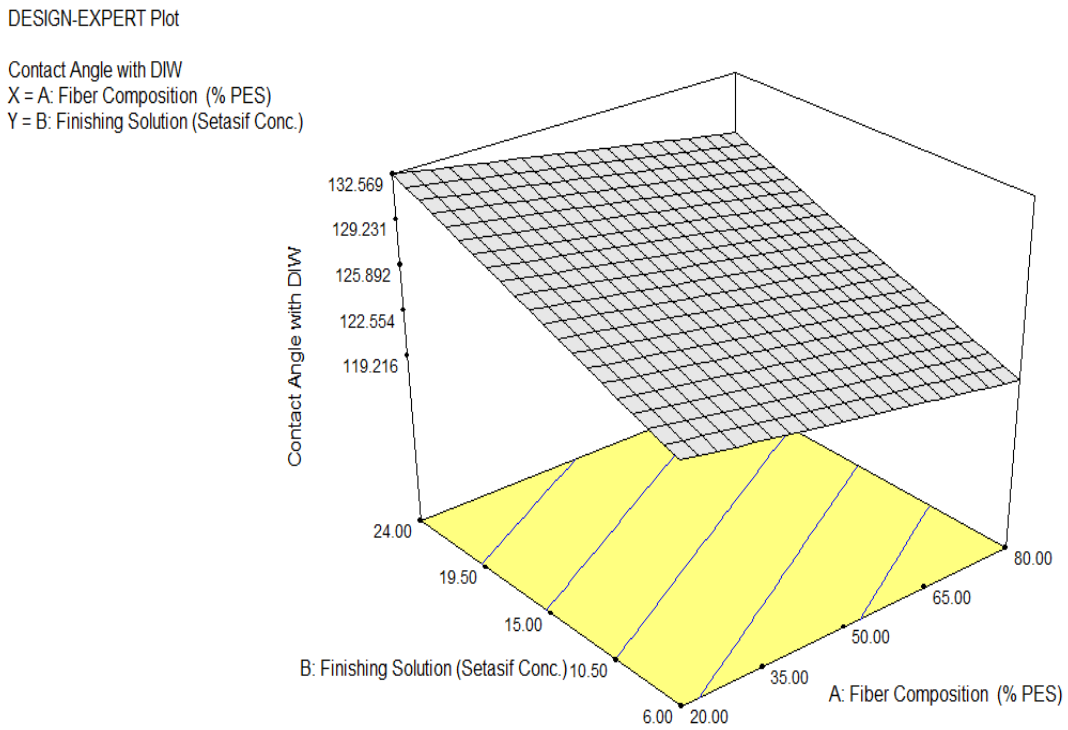


Figure 2.4. The contact angle of DI water on textile samples having different fiber composition and treated with different concentration of silicon in finishing solution

2.3.2.1.1.3. **Contact Angle with Acacia Oil (Degrees)**

The contact angles of essential oils have been measured in a similar manner as with DI water. Eucalyptus oil and lavender oil were initially used to start the evaluations however, both oils were observed to be absorbed by the textiles in milliseconds which did not allow the measurement of a stable contact angle value. Instead, the acacia oil was used, which retained a droplet long enough on the textiles to be able to measure the contact angle. This behavior can be attributed to the surface tensions of the essential oils given in **Table 2.4** which shows that the acacia oil has the highest surface tension among them which can be the reason that let us measure its contact angle on the textile samples which also demonstrates resistance to staining.

Table 2.4. Surface Tensions of Bioactive oils (using ring method)

Oil	*Surface Tension (mN/m)*
Eucalyptus Oil	26
Lavender Oil	23
Acacia Oil	33

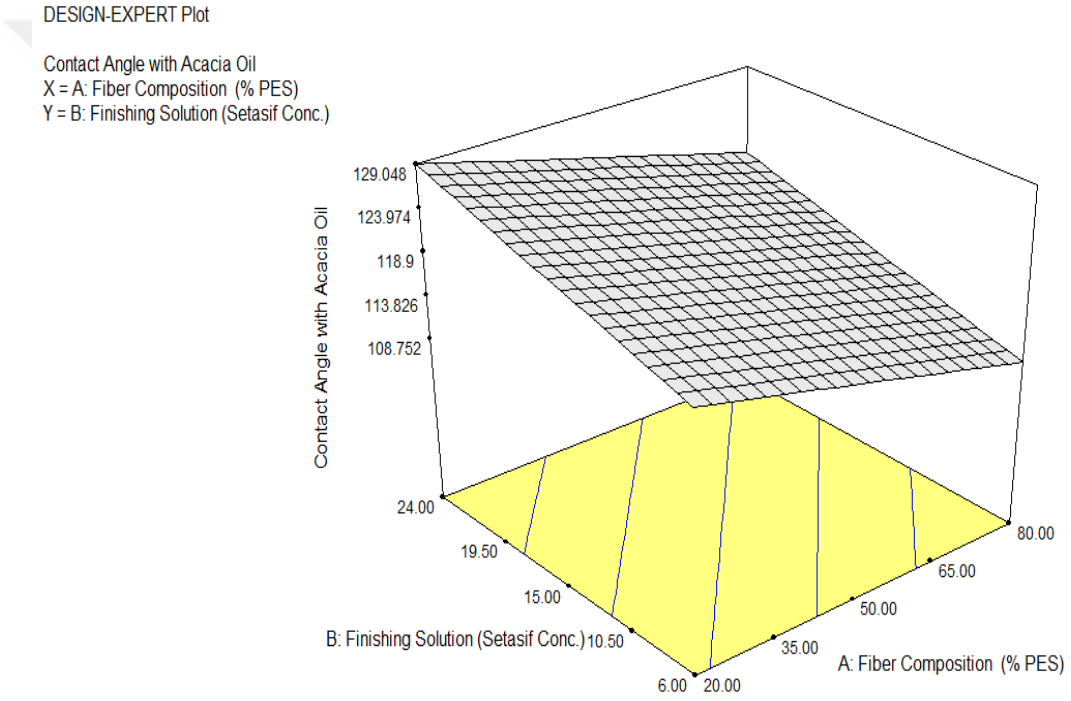


Figure 2.5. Contact angle of acacia oil on textile samples having different fiber composition and treated with different concentrations of silicon in Finishing solution

The contact angle of acacia oil on textile samples having different fiber composition and treated with different concentration of silicon in finishing solution are plotted in **Figure 2.5**.

The contact angle measurement results obtained with the acacia oil showed a similar to the responses obtained with the DI water with slightly lower angles. The observations on the eucalyptus and lavender oils, however, demonstrated higher hydrophobic behavior of the textiles due to rapid absorption of these oils for any selected fiber composition and silicon concentration in the finishing solution.

2.3.2.1.1.4. **Surface Charge [Zeta Potential (mV)] Measurements**

The effect of fabric content and silicon concentration in the finishing solution on the zeta potential of textile surfaces can be seen in **Figure 2.6** and **Figure 2.7**. **Figure 2.6** shows the Zeta potential of the textile samples having different fiber compositions and treated with different concentration of silicon in finishing solution at the pH of the finishing solution (3.52). While **Figure 2.7** shows the zeta potential values obtained at the pH of DI water. It has been observed that the effect of fabric composition is more pronounced factor in changing (more negative) the surface charge as compared to silicon concentration in the finishing solution.

It can be seen in both of the figure that textile samples with more cotton content and treated with higher concentration of silicon in the finishing have less negative surface charge, which would result in higher amount of hydrophobic capsules attachment to textile surfaces through hydrophobic-hydrophobic interactions.

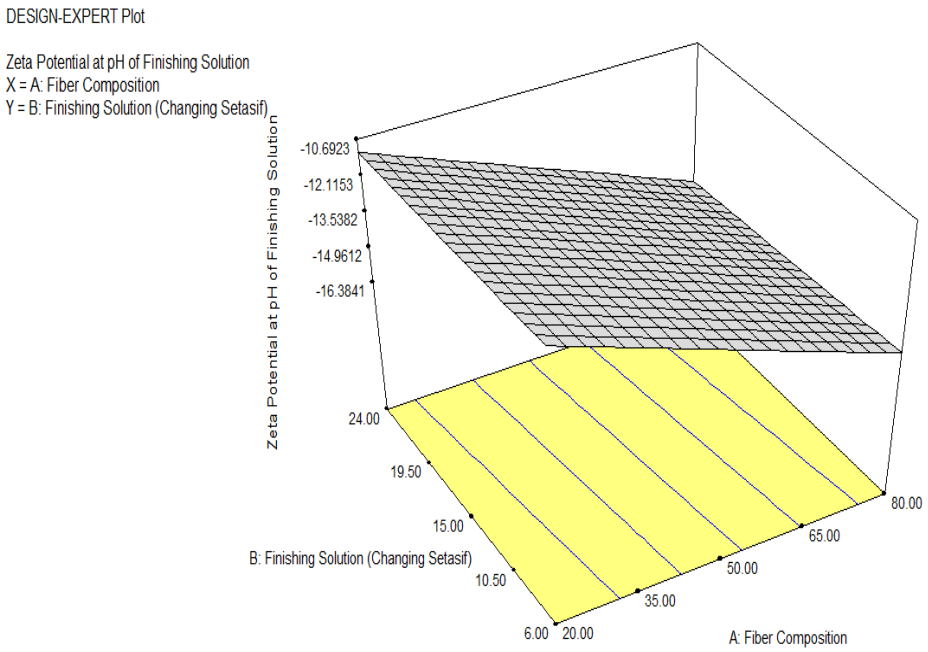


Figure 2.6 Zeta potential of textile samples having different fiber composition and treated with different concentration of silicon in finishing solution at the pH of finishing solution i.e. 3.52

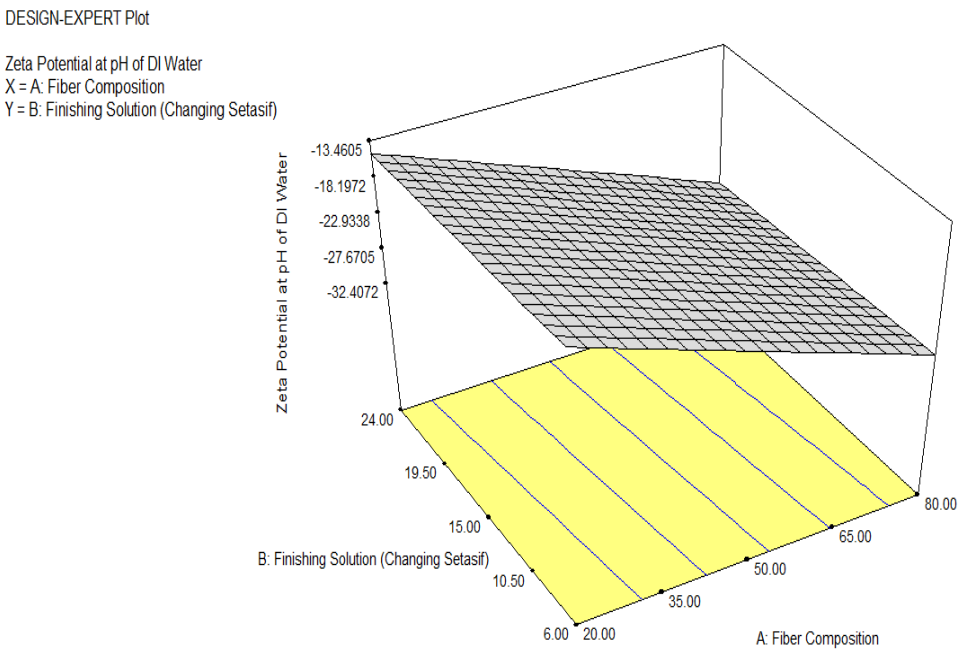


Figure 2.7 Zeta potential of textile samples having different fiber composition and treated with different concentration of silicon in finishing solution at the pH of DI water i.e. 5.87

2.3.2.1.1.5. **Isoelectric Point (IEP)**

Figure 2.8 reports the isoelectric point values of the textiles with selected fiber blends treated with different concentrations of silicon in the finishing solution. As expected the isoelectric points should shift relative to baseline, they have been found independent of the silicon concentration and only depend on the type of the fiber used in manufacturing of the textiles.

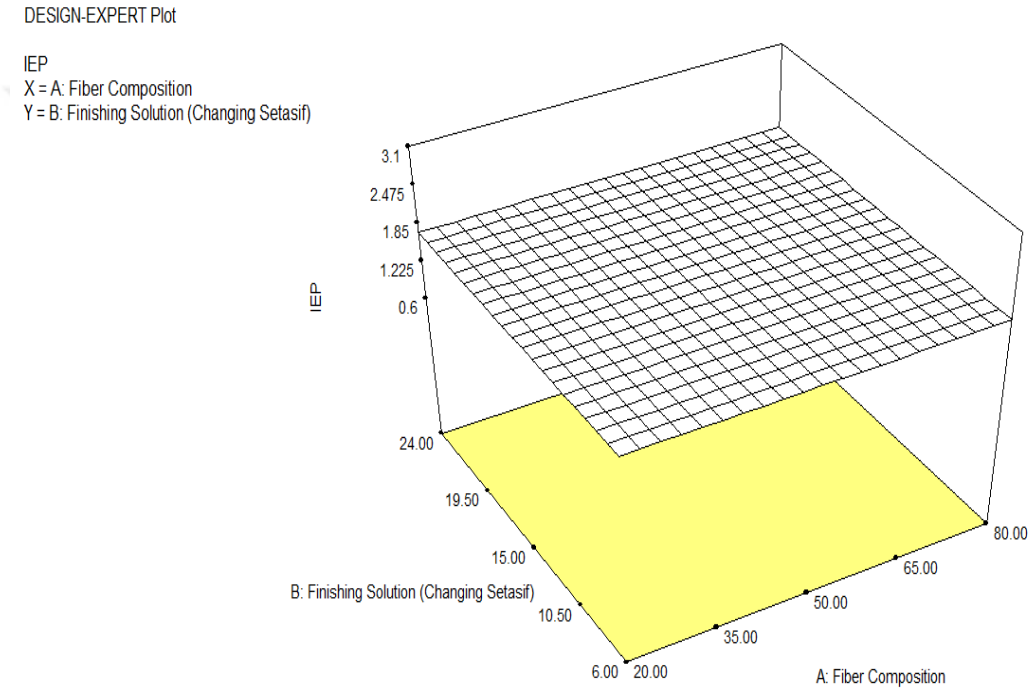


Figure 2.8 Isoelectric points of textiles having different fiber composition and finished with different concentration of finishing solution

2.3.2.1.2. **Optimization**

Based on the information presented above the desirability was evaluated for three different blends (i) 100%PES, (ii) 50%PES_50%Cotton and (iii) 100% Cotton, while keeping the factor; silicon concentration in the finishing solution the same for all the three of them.

Table 2.5 Desirability of textile blends after optimization of responses

#	*Fiber Composition (%PES)*	*Finishing Solution (Changing silicon*	*Contact Angle with DIW*	*Zeta Potential at pH of DI Water*	*Desirability*
1	100	30.00	131.57	-22.87	0.59
2	50	30.00	131.57	-22.88	0.74
3	0.00	26.09	133.80	-9.45	0.97

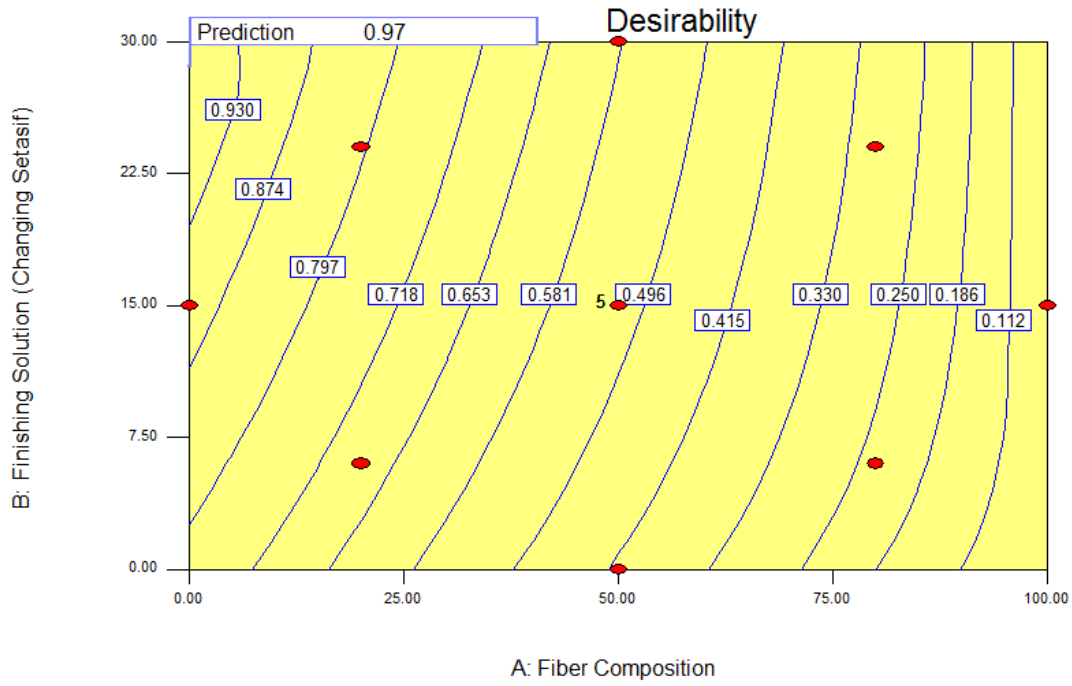


Figure 2.9 Desirability (for 100% Cotton) vs. Fiber Composition and silicon concentration in finishing solution

Table 2.5 shows the desirability of all the three blends while **Figure 2.9** shows that the higher the concentration of the silicon in the finishing solution and the higher the cotton content in the fabric the more desirable it is.

2.3.3. Attachment of capsules to textiles as per design of experiment

The capsules attachment to textiles was measured by the difference in weight of the textiles before and after spraying the capsules on them. Figure 2.10 shows that the attachment of capsules measured by weight difference is well in agreement with the prediction by the design of experiment.

From **Figure 2.10** it can clearly be understood that the higher the cotton content in the fabric and the higher the silicon concentration in the finishing solution the higher will be the capsules' attachment. This higher attachment of capsules to textile surfaces can be attributed to the higher amount silicon adhered to the textiles which results in lower negative surface charge on textile surfaces and hence less repulsive forces between the textile surfaces and hydrophobic capsules.

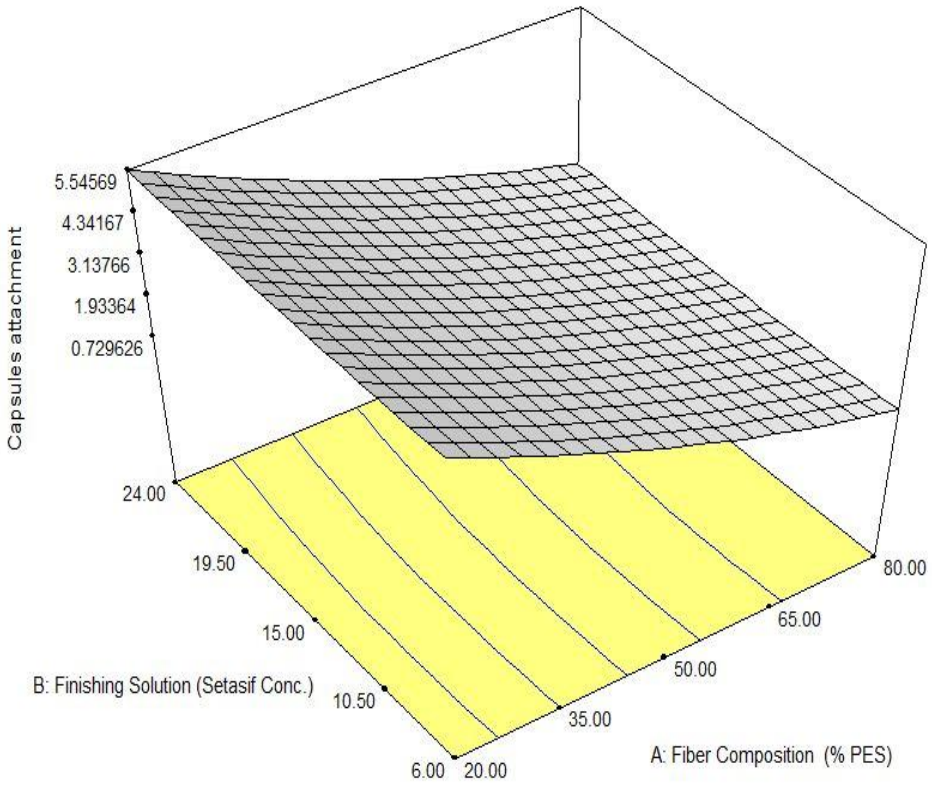


Figure 2.10 Surface plot in DoE for Capsules' attachment

Therefore, 100% cotton treated with the highest concentration of silicon in the finishing solution was selected, however based on the necessity for optimum capsules' attachment and easy ironing at lower temperatures a blend of cotton and polyester treated with highest concentration of silicon in the finishing solution was decided on, to be the most suited combination. The blend has %65cotton while %35polyester, with cotton being weaved on top for maximum capsules attachment while polyester at the bottom surface to provide ease for ironing.

2.4. Conclusion

Initially five different textiles i.e. %100 Carded cotton, %100 Combed cotton, %100 PES, %100 Viscose and %100 Tencel 100% were studied in detail. The study revealed that the cotton, polyester and their blends were better candidates as compared to the others because of their unique hydrophobic properties and wide availability in the textile industry.

A design of experiment (DoE) using response surface central composite model was used to study the surface properties of the textile as a function of the following two factors.

i. Fabric composition (%polyester content)
ii. Concentration of silicon in the finishing solution

The DoE revealed 13 tests to be carried out in order to have optimized hydrophobic properties and microcapsule adherence to textile's surfaces. The responses studied in the DoE include.

i. Change in Weight Per Unit Area (g/m^2)
ii. Contact Angle with DI_Water (Degrees)

iii. Contact Angle with Acacia Oil (Degrees)

iv. Surface Charge [Zeta Potential (mV)] measurements at the pH of finishing solution

v. Surface Charge [Zeta Potential (mV)] measurements at pH of DI Water

vi. Isoelectric Point (IEP)

The optimization of the responses in DoE was focused on more hydrophobic and more negatively charges surfaces of the textile samples. The optimization suggested 100%cotton treated with the highest concentration of silicon in the finishing solution to be the most suited combination of the two factors. However, based on the necessity for optimum capsules' attachment and easy ironing at lower temperatures a blend of cotton and polyester was selected.

The selected blend is called "Melody" in the textile industry and has %65cotton and %35polyester fiber content, and for the purpose of achieving higher hydrophobicity it has to be treated with the highest concentration of silicon in the finishing solution. The melody fabric [65%cotton/35%polyester] however, in our case, is weaved in different style i.e. cotton being weaved on top for maximum capsules attachment while polyester at the bottom surface to provide ease for ironing.

CHAPTER III

PREPARATION & CHARACTERIZATION OF MICRO/NANO-CAPSULES AND THEIR DECORATION ON TEXTILES

3.1. Introduction

Microencapsulation is the packaging of small particles or droplets of liquid with a thin film. The typical microcapsule's size ranges from 1μm to 1mm. These microcapsules consist of a core and a wall (or shell). The configuration of the core can be a spherical or irregular particle, liquid-phase suspended solid, solid matrix, dispersed solid, and aggregates of solids or liquid.

Microcapsules can be classified into three of the following morphology.

i. Mononuclear
ii. Polynuclear and
iii. Matrix types

Mononuclear (core-shell) microcapsules contain a shell around the core, while polynuclear capsules have many cores enclosed within the shell. In matrix encapsulation, the core material is distributed homogeneously into the shell material. In addition to these three basic morphologies, microcapsules can also be mononuclear with multiple shells, or they may form clusters of microcapsules.

This chapter describes different methods of PEG-b-PCL, melamine and polyurea nano-micro-capsules preparation, their characterization and decoration on textile's surfaces. The prepared nano-micro-capsules empty as well as with eucalyptus oil encapsulated were characterized in terms of their size distribution, surface morphology, surface charge, and UV-Vis absorption and surface tension measurements at different temperature. The attachment of the capsules to textile has been studied by weight difference before and after treatment with capsules. Moreover the presence of the capsules has been investigated by scanning electron microscopy (SEM) before and after 1 and 5 washing cycles.

3.2. Experimental

3.2.1. Preparation of the micro/nano capsules

3.2.1.1. PEG-b-PCL based micro/nano capsules

PEG-b-PCL based capsules were prepared using solvent evaporation technique. In this method polymer is dissolved in volatile solvents and emulsions are formulated. PEG-b-PCL was dissolved in acetone (0.76mg/ml: critical micelle concentration) in a beaker on a magnetic stirrer for 24 hours. The prepared solution was then added to DI water drop by drop (10ul) while the DI water was kept stirred at 600rpm. **Figure 1.5** shows the schematic of PEG-b-PCL capsules' synthesis process.

3.2.1.2. Commercially available: Melamine based capsules

The general preparation procedure of melamine microcapsules is as follows. Melamine (0.2 M) and 37% formaldehyde (0.6 M) in 50 mL of distilled water were adjusted to pH 8.8 ± 0.1 using 0.5M NaOH solution. After the Tween 20 (2%, w/v) was dissolved in 50 mL of distilled water, peppermint oil was added to the solution.

Microencapsulation of essential oil was conducted in a 500-mL four-neck flask via in-situ polymerization. After the addition of 0.002 M of PVA as a protective colloid, the M-F prepolymer attached to the surface of the peppermint oil was cross-linked, and then solidified via pH control. After the completion of the microencapsulation reaction, the resultant microcapsules were collected and washed in 30% (w/v) ethanol solution and distilled water (Hwang, 2006).

3.2.1.3. Commercially available: Polyurea based capsules

Polyurea microcapsules have been prepared using oil in water emulsion technique in which the aqueous phase is composed of 170 mL of deionized water containing 0.5 %wt of Tween 80 as emulsifier, whereas the organic phase is a mixture of essential oil (eucalyptus oil) and isocyanate monomer (TDI and/or PPI in appropriate ratio), dissolved in the minimum volume of PA. The two phases are emulsified at room temperature at 3000 rpm. Then, the second monomer (HH, EDA, or BDA), previously diluted in 30 mL of deionized water, is added to the emulsion and the system is left to react for 3 h under agitation at 150 rpm. The resultant microcapsules slurry is filtered, washed two-three times with water, and left to dry at room temperature. (Paola, 2007).

3.2.2. Characterization of capsules

PEG-b-PCL, commercially available melamine and polyurea-based capsules were characterized in terms of their size distribution, surface morphology, surface charge, and UV-Vis absoption and surface tension measurements at different temperature. The attachment of the capsules to textile has been studied by weight difference before and after treatment with capsules. Moreover the presence of the capsules has investigated by scanning electron microscopy (SEM) before and after 1 and 5 washing cycles.

3.2.2.1. Atomic Force Microscopy

The surface morphology of the capsules has been investigated with Nanomagnetics Instruments Atomic Force Microscope (AFM) using tapping mode. A 3 µl droplet of samples was deposited on a freshly cleaved mica surface, spread on and dried at room temperature 25°C.

3.2.2.2. Size measurements with Coulter LS-13 320

The capsules size measurements were performed, to investigate their stability, via light scattering technique using Coulter LS-13 320 Laser Diffraction Particle Size Analyzer (Beckman Coulter ALM-aqueous Liquid Module) instrument. In the process of particle size measurements DI water at pH 6 was used as background. The capsules' solutions were added drop by drop to the background until the Polarization Intensity Differential Scattering (PIDS) reached 50%. Three successive runs (tests) were carried out to validate the reproducibility of the capsules' size measurements.

3.2.2.3. Size measurement with DLS

The biodegradable polymeric nanocapsules (PEG-b-PCL) synthesized at different stirring speeds were analyzed for their size distribution to investigate the effect of stirring speed on their size distribution. The nanocapsules prepared were sonicated for 3 minutes before sampling. Particle size measurements were carried out at pH 6 using Malvern Nano ZS Analyzer. The refractive index measured experimentally was found to be 1.3372 and was used in the program settings of Malvern Nano ZS Analyzer's software for size measurements.

3.2.2.4. Surface Charge Measurement

The zeta potentials (mV) of the polymeric capsules prepared at different RPM were measured by using Malvern Nano ZS Analyzer. The surface charge has been measured at pH 6.

3.2.2.5. Empty and loaded capsules' Size and Zeta Potential comparison

The biodegradable polymeric nanocapsules synthesized at different stirring speeds were analyzed for their size distribution. The size and zeta potential of both the empty and loaded with eucalyptus oil nanocapsules were measured using Malvern Nano ZS Analyzer. Both capsules were prepared at room temperature and 800 rpm using a droplet size of 10μm.

3.2.2.6. Volume calculations from capsules' size measurement with Coulter

Statistics from the volume% of size measurements of PEG-b-PCL nanocapsules with Coulter have been used to calculate the volume of the capsules present in 20ml of the capsules' solution. From measuring this volume the capacity of the capsules' to encapsulate essential oils has been determined.

3.2.2.7. Volume and surface area comparison of capsules from capsules' size measurement with Coulter

The volume and surface area of PEG-b-PCL, polyurea and melamine were calculated from their volume% of size measurements with Coulter LS 13 320. The volume and surface area of the different capsules has been determined in order to be able to understand the coverable area of the textile surfaces with the capsules having eucalyptus oil encapsulated in them.

3.2.2.1. Controlled Release of Eucalyptus oil

UV-Vis spectra of the capsules loaded with eucalyptus oil at different temperatures were collected using Schimadzu 1280 UV-Vis spectrometer with wavelength range set to 190-1100nm. The samples were heated from room temperature (25 °C) to 30, 40, 50 and 60 °C before collecting their UV-Vis absorption spectra.

In another attempt to study the controlled release 2mM methylene blue was encapsulated in PEG-b-PCL capsules and was investigated for UV-Vis absorption at different temperatures.

Controlled release of eucalyptus oil from the capsules has also been studied by measuring surface tension of the capsules' solution after heating at different temperatures. The surface tension has been measured with Attension theta light optical goniometer using falling drop method. The solutions were heated from room temperature (26 °C) to 30, 35, 45 and 60 °C and were then left to cool to room temperature before measuring their surface tensions.

3.2.3. Decoration of the textiles with capsules

3.2.3.1. Dip Coating

The dip-coating, of textiles, is a continuous process involves immersion, start-up, deposition, drainage, and evaporation. **Figure 3.1** shows the schematic of dip coating process through which the textile sample has been coated in Kivanc Textiles, Adana, Turkey.

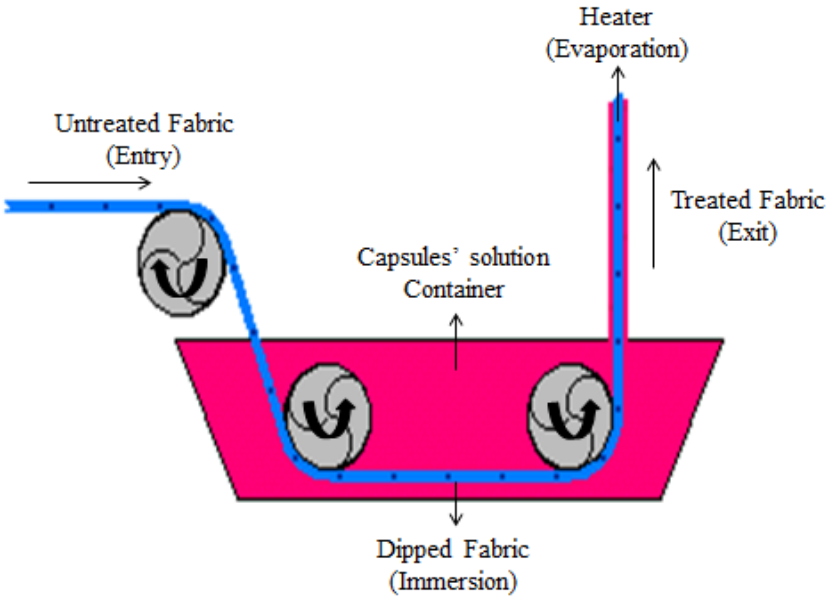


Figure 3.1. Schematic of dip coating of textile (Eikos, 1996)

All the steps involved in dip coating are carried out directly one after the other and are briefly described below.

i. Immersion: The textile is immersed in the capsules' solution at a constant speed'
ii. Start-up: The textile is pulled through the solution container.
iii. Deposition: The thin layer deposits itself on the textile while it is pulled up.
iv. Drainage: Excess liquid will drain from the surface.
v. Evaporation: The solvent evaporates from the textile leaving the capsules adhered to the textile.

3.2.3.2. Spray Coating

Spray coating system is relatively simple and results in almost no waste of capsules. In a spray coating system the capsules' solution is applied to textile surfaces by pressurizing the solution through a nozzle i.e. a pressurized liquid flows through a small orifice. The pressure built up in the nozzles generates droplets with high velocities and deposit the capsules on the textile surfaces.

Spray coating of the textiles in our case is suggested to be done by end user i.e. a solution having eucalyptus oil encapsulated in biodegradable capsules and some free eucalyptus oil is to be sprayed on the garments, when needed.

3.2.3.3. Scanning electron microscopy

The surface topography of the treated textiles (a) unwashed, (b) after 1 washing cycle and (c) after 5 washing cycles was examined using SEM (Hitachi SU70) fitted with an EDS detector (Joel, Oxford Instruments). 1 washing cycle means 45 minutes of washing in a beaker with water on a magnetic stirrer. The samples were treated by spraying with PEG-b-PCL capsules on cotton side and were left to dry at room temperature. Samples were attached to the SEM holder using a double-sided carbon adhesive tape (Agar Scientific). A gold coating of 25nm thickness was sputtered on the samples using a High Vacuum Sputter (Emitech K550), for providing optimal conductivity.

3.2.4. Antitick and antimicrobial activity of eucalyptus oil

The antitick/antimicrobial activity of eucalyptus oil was investigated at one of the project's collaborator facility (National Institute of Public Health (NIPH) Prague, Czech Republic). Common ticks were collected in the field by flagging method and were stored in plastic vials with grass leaves. The antitick activity was evaluated by the different methods such as circular test on carton, circular test with treated textiles, Caroll's test on human skin and treated textile, fall off ticks from treated textile surface, forced contact method. Additionally the repellency of Eucalyptus and Levander oil for female ticks (*Ixodes ricinus*) on human skin was evaluated by exposing the ticks to treated skin and letting them crawl for 5 minutes.

3.3. Results and Discussion

3.3.1. Characterization of capsules

3.3.1.1. Atomic Force Microscopy (AFM)

The AFM images of PEG-b-PCL capsules (as prepared), melamine and polyurea based capsules (diluted to match the biological capsule concentration) are given in **Figure 3.2** with the cross sections of the capsules, respectively.

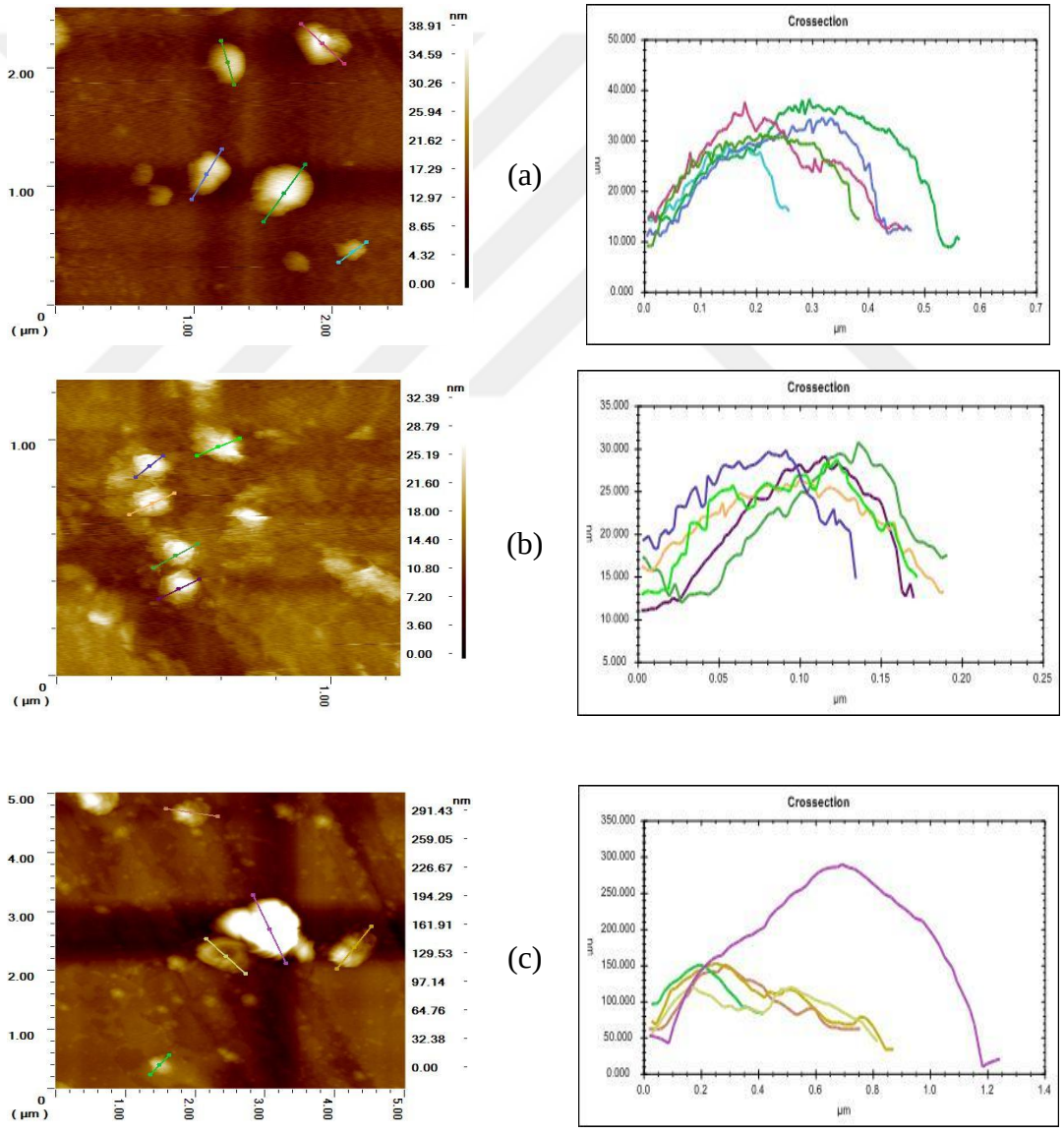


Figure 3.2. AFM images and cross section analyses for (a) PEG-b-PCL, (b) melamine and (c) polyurea based capsules

The AFM images show that there is agglomeration in PEG-b-PCL and polyurea based capsules while there is, almost, no agglomeration in melamine capsules and have been found to be, relatively, more stable. This observation is confirmed in the size measurement of the capsules with Coulter LS 13 320.

3.3.1.2. Size measurements with Coulter LS-13 320

The capsule size measurement analysis using Coulter LS-13 320 is reported in **Figure 3.3**.a through 3.4.c by volume percent and number percent distributions for three overlaying runs of PEG-b-PCL, melamine and polyurea based capsules, respectively.

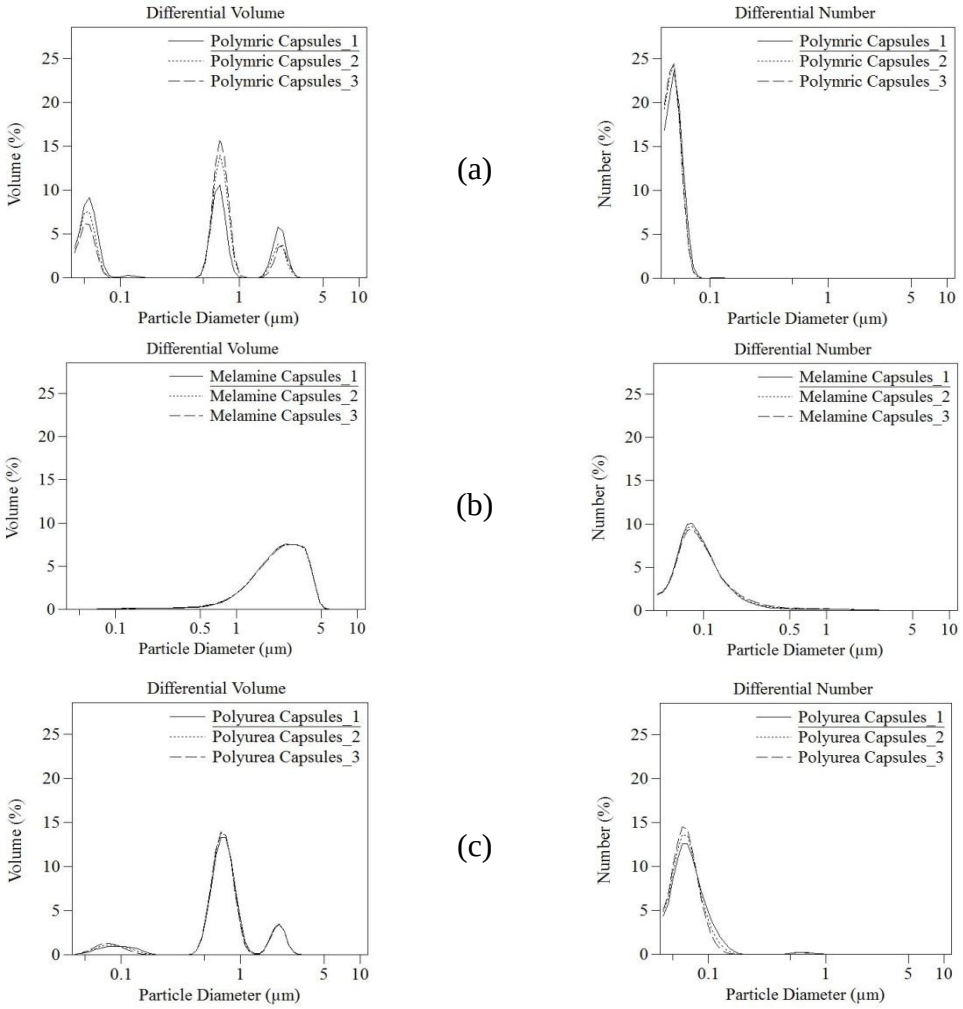


Figure 3.3. Static light scattering particle size measurement results for (a) PEG-b-PCL, (b) melamine and (c) polyurea based capsules measured by %Volume and %Number distributions

In the images above it can be clearly seen that the %Volume distribution for PEG-b-PCL and polyurea based capsules possess three peaks which means there is agglomeration or some large capsules while melamine capsules have a single peak meaning that melamine capsules are uniform in size and are more stable. However, the %Number distribution for all the three capsules types show that the agglomeration or the large size capsules are not significant parts of the overall size distribution.

The average capsule size from %Number distribution are 50nm, 83nm and 70nm for PEG-b-PCL, melamine and polyurea based capsules respectively which are well in agreement with size measured using AFM.

3.3.1.3. Size measurement using Dynamic Light Scattering

The average size, using DLS, of three runs carried out for each sample prepared at different stirring speed is reported in **Figure 3.4** below. It has been found that the stirring speed during capsules' synthesis affects size of the capsules formed. From stirring speed of 300 to 700 rpm the nanocapsule size increases while from 700 to 900 rpm it decreases linearly.

3.3.1.4. Surface Charge Measurement

Figure 3.5 shows the zeta potential of empty capsules formed at different stirring speeds. The zeta potential values represent the same trend as the size distribution of the capsules.

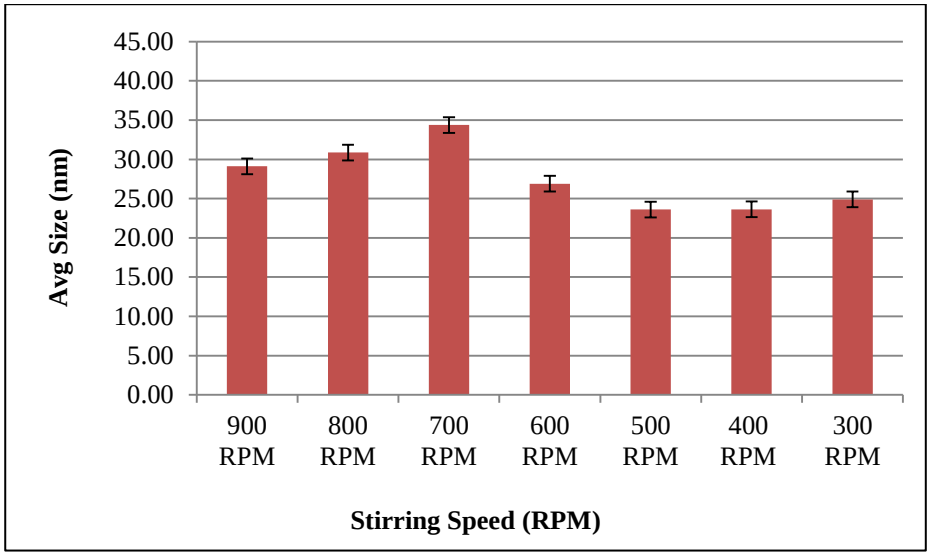


Figure 3.4. Size distribution of empty capsules meaured by dynamic light scattering formed at different stirring speeds

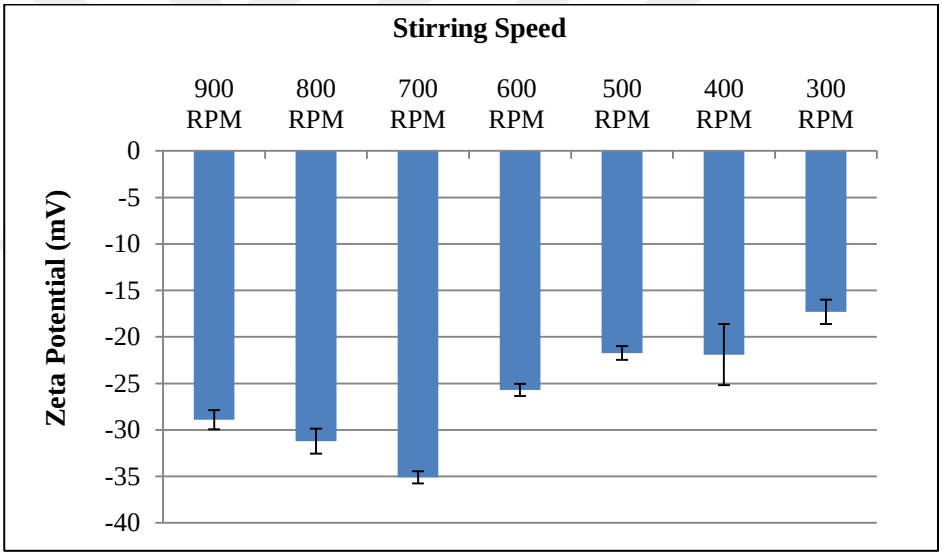
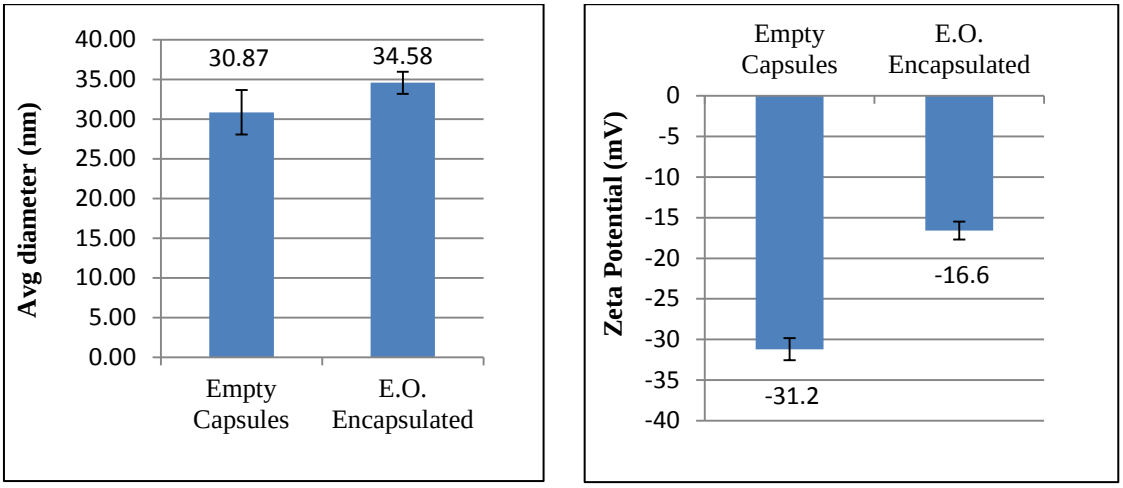


Figure 3.5. Surface charge of empty capsules formed at different stirring speeds

3.3.1.5. Empty and loaded capsules' Size and Zeta Potential comparison

The size and zeta potential measurements of nanocapsules, empty and eucalyptus oil loaded, prepared at room temperature and stirring speed of 800 rpm are reported in **Figure 3.6**. The capsules having eucalyptus oil encapsulated in them were found to be larger in size and having less negative zeta potential, which can be attributed to the presence of eucalyptus oil in them.



(a) (b)

Figure 3.6. Comparison of (a) size and (b) Zeta Potential of empty and loaded capsules prepared at room temperature and 800 rpm stirring speed

3.3.1.6. Volume calculations from capsules' size measurement with Coulter

Statistics from the %volume size distribution of three successive runs for PEG-b-PCL nanocapsules with Coulter were used to calculate the total volume of nanocapsules present in 20 ml of polymeric micelles' solution. **Table 3.1** below summarizes the results obtained by processing %Volume statistics of PEG-b-PCL from Coulter and has been found that the average volume of capsules present in 20ml solution is nearly $1um^3$. This volume is validated in surface tension measurements which gives us an optimal volume of eucalyptus oil that can be encapsulated in 20 ml of micelles' solution (at single CMC) of $1um^3$.

Table 3.1. Volume calculations form % volume measurements of polymeric capsules.

Run #	*Volume (%)*	*Volume (um^3)*
1	99.97	1.040
2	99.99	0.742
3	99.93	0.760
Avg. Vol.	99.97	0.850
S.D.	0.02	0.167

3.3.1.7. Volume and surface area comparison of capsules from capsules' size measurement by Coulter LS 13 320

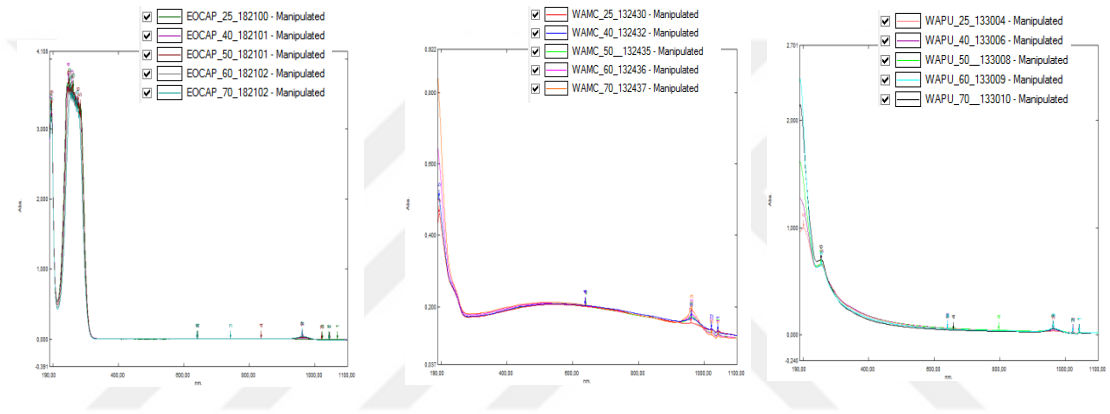
From the volume and surface area comparison, given in **Table 3.2**, it can be seen that the, for the same concentration, volume of PEG-b-PCL nanocapsules is more than 10 times higher than melamine and polyurea capsules while the its surface area 100 times higher than polyurea and melamine capsules. Therefore, treating the textile with PEG-b-PCL nanocapsules will result in covering more surface area and more eucalyptus oil will be present on the textile's surfaces.

Table 3.2. Volume and surface area comparison of selected capsules

Sample	*Volume (μm^3)*	*Surface Area (μm^2)*
PEG-b-PCL Capsules	0.03467	0.14433
Melamine Capsules	0.00411	0.00818
Polyurea Capsules	0.00020	0.00044

3.3.1.8. Controlled Release of Eucalyptus oil

The UV-Vis absorption spectra of PEG-b-PCL, and diluted solutions of melamine and polyurea based capsules are shown in **Figure 3.7** (a), (b) and (c), respectively. The spectra show that there is no substantial change in the absorption of UV-Vis light, which in turn means that there is no, or very less amount of, eucalyptus oil released, with temperature. This no change in UV-Vis absorption can also be attributed to the fact that there is no UV-Vis peak for eucalyptus oil itself.



(a) (b) (c)

Figure 3.7. UV-Vis absorption: (a) PEG-b-PCL capsules (b) melamine and (c) polyurea based capsules

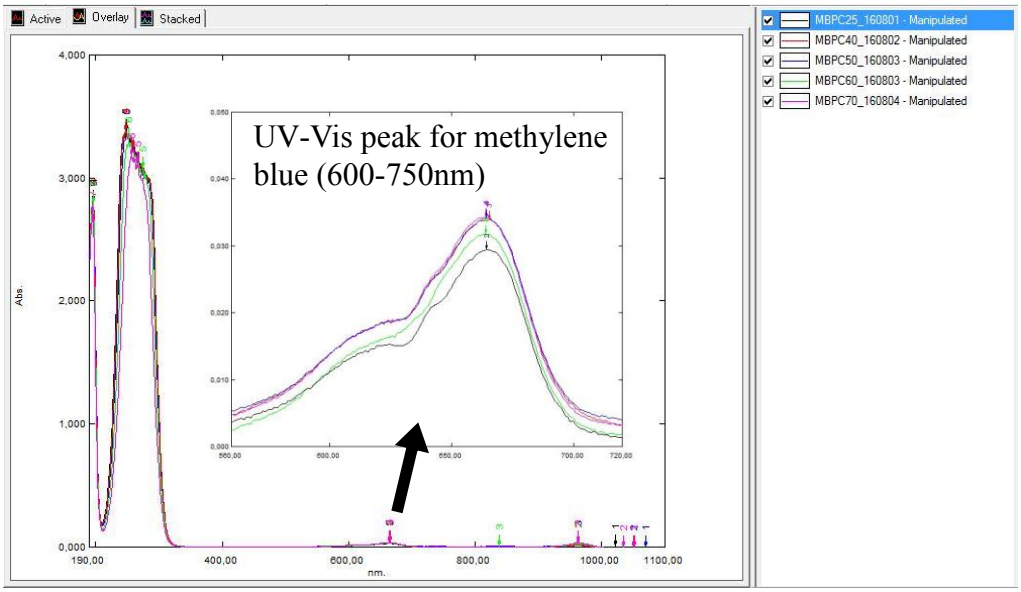


Figure 3.8. UV-Vis absorption of PEG-b-PCL loaded with methylene blue

Figure 3.8. UV-Vis absorption of PEG-b-PCL loaded with methylene blue **Figure 3.8** shows the UV-Vis absorption spectra of PEG-b-PCL loaded with methylene blue. No significant change in UV-Vis absorption has been observed in the UV-Vis absorption. However the UV-Vis absorption has shown an increase for methylene (magnified). This insignificant change can be due to the less volume of 2mM methylene blue encapsulated in PEG-b-PCL.

The UV-Vis absorption studies of capsules have not resulted in conclusive findings to quantify the controlled release; therefore surface tensions of the capsule's solutions have been measured as alternative way of studying the controlled release of eucalyptus oil. The surface tension of capsules, after heating to 30, 35, 45 and 60 °C and then letting them cool to room temperature, is given in **Figure 3.9.**

There is a decrease in the surface tension after heating to 30 °C which can be attributed to the release (or presence of free eucalyptus oil), of eucalyptus oil from the capsules. The surface tensions measured after the other heating steps have shown a linear increase, which can be attributed to the less amount of eucalyptus oil present in the capsules. However, the amount of eucalyptus oil release could not be quantified.

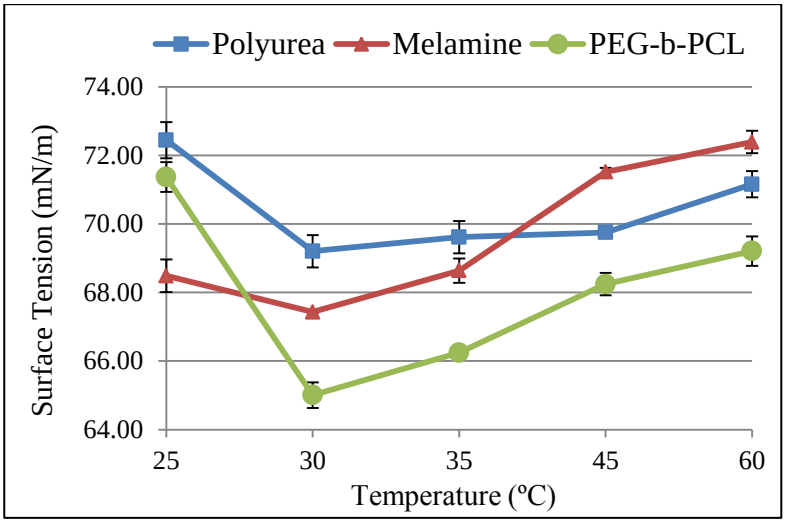


Figure 3.9 Surface tension measurements of capsules loaded with eucalyptus oil after heating at different temperatures

3.3.2. Development/decoration of the textiles with capsules

3.3.2.1. Attachment of capsules to textiles as per design of experiment

The capsules attachment to textiles' surface as a function of fabric content and silicon concentration in the finishing solution is given in **Figure 3.10**. The attachment results show dependency on both the factors and the more attachment of capsules to the textiles' surface can be achieved when the fabric is more cotton fiber rich and is treated with higher silicon concentration in the finishing solution. Moreover the capsules attachment results measured by weight difference, before and after treatment, have been found well in agreement with the results obtained in the optimization of the responses in the design of experiment.

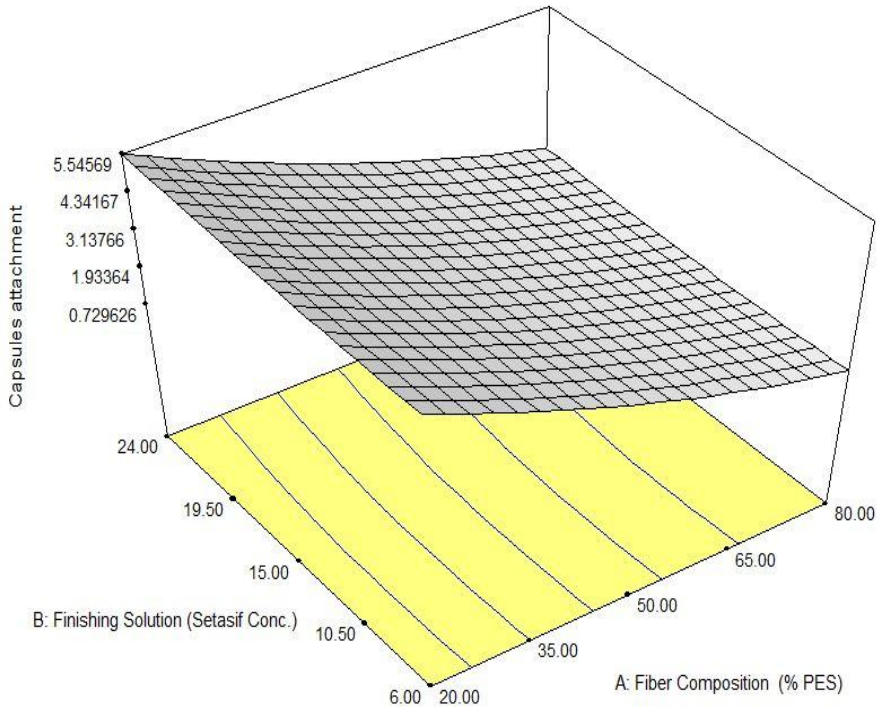


Figure 3.10 Attachment of capsules to textile surfaces

3.3.2.2. Scanning electron microscopy (SEM)

The SEM images of the treated textiles (a) unwashed, (b) after 1 washing cycle and (c) after 5 washing cycles are given in **Figure 3.11** (a), (b) and (c) respectively. Unwashed sample has been used as a reference to investigate the presence of capsules after washing. **Figure 3.11** (b) and (c) below show that there are still some capsules left after washing the textiles' sample which means that the textile can retain the capsules for a prolonged period of time

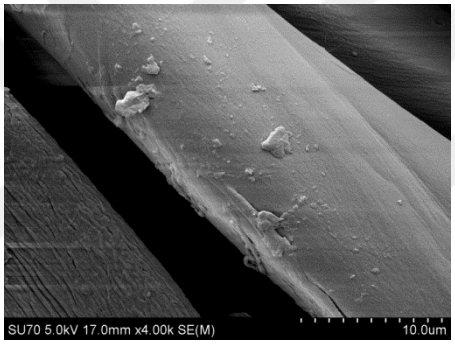
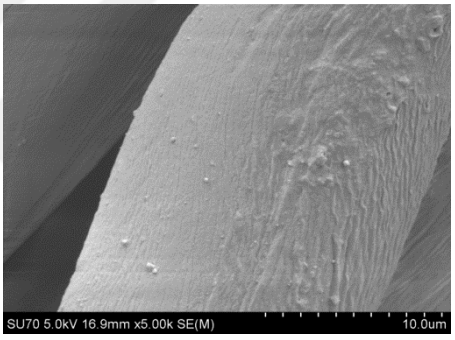
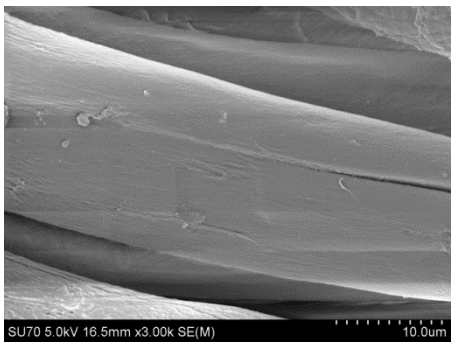
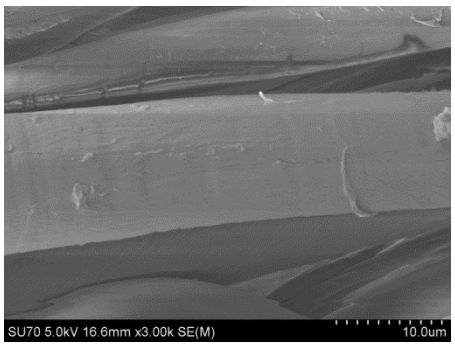
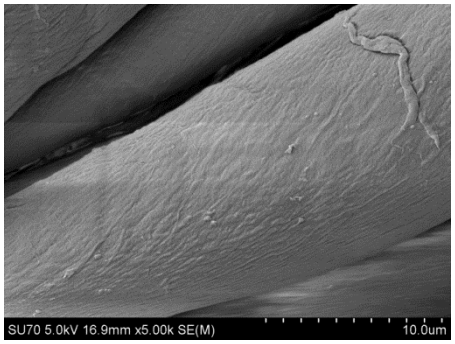
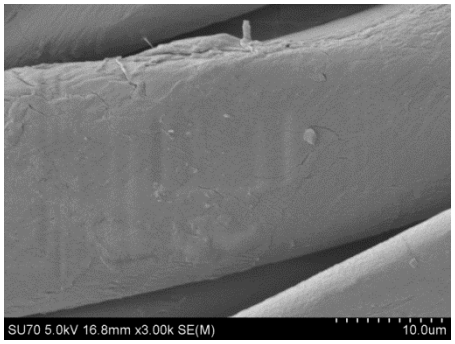
Washing Cycles #	Treated with	
	Empty Capsule	Eucalyptus oil loaded capsules
0		
1		
5		

Figure 3.11 SEM images of reference: after 0 wash cycle i.e. unwashed, Sample after 1 wash cycle and sample after 5 wash cycles

3.3.3. Antitick and antimicrobial activity of Eucalyptus oil

Eucalyptus oil exhibit high antitick efficacy which can be seen in **Table 3.3** however further evaluation of the alternative efficiency test methods is also needed to have a better understanding of tick repellency of eucalyptus oil as the results at hand are not sufficient for a clear evaluation of efficacy against ticks.

At the same time Eucalyptus oil was tested against 3 pathogenic fungi cultures according to the International Standard ISO 20743:2007 by INCDTP, Romania. The first test results are promising and show the very good antifungal activity.

Eucalyptus oil encapsulated in nanoliposomes have shown good antibacterial activity (Lin, 2015) plus from our own above results we can conclude that eucalyptus oil is active against ticks and fungi and bacteria and decided to use it as our antimicrobial agent for TickoTex.

Table 3.3 Tick repellency (%) of Eucalyptus and Lavender oil

Oil	*Dilution*	*Time after application (Minutes)*	*No of test*	*Repellency (%)*
Eucalyptus	1:19 (0.05mg/cm2)	5	10	70
Eucalyptus	1:49 (0.02mg/cm2)	5	10	20
Levander	1:19	5	10	60
Levander	1:49	5	10	20

3.4. Conclusion

PEG-b-PCL capsules were synthesized using solvent evaporation technique while melamine and polyurea nano-micro-capsules were obtained from commercial suppliers. All the three types of capsules were characterized in terms of their size distribution, surface morphology, surface charge, and UV-Vis absorption and surface tension measurements at different temperature.

The UV-Vis absorption studies of the capsules have not resulted in conclusive findings to quantify the controlled release; therefore surface tensions of the capsule's solutions have been measured as alternative way of studying the controlled release of eucalyptus oil. The surface tension of capsules, after heating to 30, 35, 45 and 60 °C and then letting them cool to room temperature, has been measured. A decrease in the surface tension of the capsules solutions, after first heating, while a linear increase, after the successive heating steps, have been observed. This change in surface tensions of the capsules solutions can be attributed to the release (or presence of free eucalyptus oil), of eucalyptus oil from the capsules. However, the amount of eucalyptus oil released could not be quantified.

The attachment of the capsules to textile has been studied by weight difference before and after treatment with capsules. The presence of the capsules has been investigated by scanning electron microscopy (SEM) before and after 1 and 5 washing cycles.

For studying the antitick efficacy of eucalyptus oil common ticks were collected in the field by flagging method and were stored in plastic vials with grass leaves. The antitick and antimicrobial efficacy was evaluated by different methods such as circular

test on carton, circular test with treated textiles, Caroll's test on human skin and treated textile, fall off ticks from treated textile surface, forced contact method. At the same time Eucalyptus oil was tested against 3 pathogenic fungi cultures according to the International Standard ISO 20743:2007 by INCDTP, Romania.

It has been found that eucalyptus oil exhibit high tick and microbial repellency. However further evaluation of the alternative efficiency test methods is also needed to have a better understanding of tick repellency of eucalyptus oil.

CHAPTER IV

MARKET AND LIFE CYCLE ANALYSES

4.1. Introduction

Life Cycle Analysis (LCA) is an emerging science in which the environmental impacts related to all the stages of a product's life from cradle to grave are evaluated. These stages include the extraction of raw material, manufacturing, distribution of the product to end user, maintenance, and disposal or recycling. Conventionally there are the following two main types of LCA.

i. Product based LCA
ii. Process based LCA

According to a study on "Life Cycle Assessment of Cotton Fiber and Fabric", conducted for VISION 21 by Cotton Incorporated and PE International, textile manufacturing and consumer use are the two main phases in the LCA of textile products. The potential impacts of textile manufacturing, due to extensive use of energy in different processes, are very high as compared to the impacts of usage of the product by consumer. In this study, the process based LCA has been used.

4.2. LCA of TICKOTEX

Conventionally there are two main types of LCA, product based LCA and process based LCA. In this study process based LCA method has been used for the life cycle analysis of the developed product: TICKOTEX.

Process based LCA means the itemization of inputs (materials and energy resources) and the outputs (emissions and waste to the environment) for a given step in producing a product. Work towards actual quantification of the parameters of the LCA method has not been achieved fully as relevant database for Turkey does not exist and primarily EcoInvent database will be used.

One of the main issues of any LCA is to be able to set the right boundaries. In this study the LCA is focused only on the process steps of the textile manufacturing process where any addition or modification of the process is needed.

4.2.1. Standard process flow of textile manufacturing

Following is the list of the production steps involved in the manufacturing of textile fabrics as used in Kıvanç Tekstil Adana, Turkey.

i. Desizing
ii. Bleaching: decolourization of greige material into a suitable material for next processing
iii. Drying
iv. Singeing: removal of the loose fibers protruding on the surface of textile
v. Mercerizing: treatment of fabric to increase its luster and affinity for dyes
vi. Rinsing
vii. Drying
viii. Polyester Optimal Fixation
ix. Optical Bleaching
x. Optical Rinsing
xi. Drying
xii. Chemical Finishing

xiii. Eucalyptus Finishing: Application of the eucalyptus finishing on the textile

xiv. Sanforizing: method of stretching, shrinking and fixing the woven cloth in both length and width before cutting and producing, to reduce the shrinkage which would otherwise occur after washing.

xv. Quality Control

Following the definition of the LCA boundaries, the LCA parameters are determined as well. In **Table 4.1** a matrix of parameters is given that includes only the processes which need a change(s) or additional process step(s) are taken into consideration in this study.

i. Chemical Finishing: Change of the chemical used

ii. Eucalyptus Finishing: Introduction of a new process step

iii. Sanforizing: change of chemical used

Table in APPENDIX A lists all the processes involved in the manufacturing of textile along with necessary process changes and/or additions for the project; TICKOTEX. However, most of these steps do not involve any chemical, energy or water change when compared to the conventional textile production and will not affect the LCA of the final product i.e. TICKOTEX.

Table 4.1. The matrix of determined parameters to be considered in LCA

Process change	*Chemical Finishing*	*Eucalyptus Finishing*	*Sanforizing*
Chemical/bio-chemical input	+	+	+
Change in the Electricity Consumption		+	
Change in Natural Gas Consumption		+	
Change in Water use and/or associated Wastewater	+	+	+

Second step in the LCA for TICKOTEX is to determine the impacts of the product use especially release to environment following washing of the product, which will be regarded as a process step. In the following project term, following the finalization of use and properties of all above parameters, quantification of LCA and its associated Life Cost Calculation (LCC) will be performed and left as a future work in this thesis.

4.3. Market Analyses

For market analysis an extensive questionnaire has prepared in which the potential target users have been interviewed to about their interests and opinions about the product. The questionnaire is provided in APPENDIX and has been shared with the contact persons of selected companies (given in **Table 4.2**).

Table 4.2. Details of the companies contacted for their response about the product

Company	*Profile*	*Contact Name*	*Position*	*Status*
Decathlon	Sports Wear & Gadgets	Selin Gülgün	Outdoor Brand Manager	Contacted /Turkey office (forwarded to France HQ) Waiting for reply
The Turkish Gendarmerie	Gendarmerie (Jandarma)	Ersin Başçavuş	Procurement Manager	Contacted Waiting for Reply
Boyteks	Outdoor fabric producer	Metin Keser / Özkan Bey	Sales Manager /Quality Manager	Contacted Agreed to reply
Adrenalin Outdoor	Outdoor Products Wholeseller	Burak Bey	Owner	Contacted Agreed to reply
Turkish Land Forces	Army	Mustafa Yarbay	Wear & Equipment Manager	Contacted Agreed to reply

Responses of the contact persons' (only who replied till now) to the questionnaire are very positive and an interest in the developed product has been shown. The findings of the interviews are summarized in the following section.

4.3.1. Findings of the questionnaire

Fabrics used:

i. Cotton and polyester are among the most commonly used fabrics.

Replenishment concept:

i. Varied, or even no, responses to the question about replenishment of the product

Concerns:

i. One common concern has been durability of product.
ii. One of the contact persons has a reservation about using cotton fabric and it is the shrinking of cotton and hard to iron.
iii. Price

Conclusion:

Overall an interest in the suggested product has been shown by the contact person both for personal use and their own customers. Since the product developed meets the needs of the customer.

The findings of our study suggests a combination of %65cotton-%35polyester treated with more silicon content in the finishing solution has the ability to maintain a higher number of capsules having antitick and antimicrobial agent in them. Moreover, polyester is synthetic fiber and is less prone to microbial attacks which makes it more durable and will also help in easy ironing of the fabric.

4.4. Conclusion

Conventionally there are the following two main types of Life Cycle Analysis.

i. Product based LCA.

ii. Process based LCA.

In this study process based LCA method has been used for the life cycle analysis of the developed product; TICKOTEX. Process based LCA means the itemization of inputs (materials and energy resources) and the outputs (emissions and waste to the environment) for a given step in the production a product. In this study work towards actual quantification of the parameters of the LCA method has not been achieved fully as relevant database for Turkey is not available and primarily EcoInvent database will be used.

One of the main issues of any LCA is to be able to set the right boundaries. In this study the LCA is focused only on the process steps of the textile manufacturing process where any addition or modification of the process is needed. Based on setting the boundaries a new a flow of processes has been proposed.

Another important factor in the LCA for TICKOTEX is to determine the impacts of the product use especially release to environment following washing of the product, which will be regarded as a process step. Following the finalization of use and properties of all the parameters, discussed above, quantification of LCA and its associated Life Cost Calculation (LCC) will be performed and left as a future work in this thesis.

For market analysis an extensive questionnaire has prepared in which the potential target users have been interviewed to know about their interests and opinions

about the product. The questionnaire is provided in **APPENDIX** has been shared with the contact persons of selected companies (given in **Table 4.2**).

Overall an interest in the developed product has been shown by the contact person both for personal use and their own customers. Since the product developed meets the needs of the customer.

CHAPTER V

CONCLUSIONS AND FUTURE RECOMMENDATIONS

5.1. General Conclusion

Tick-borne encephalitis (TBE), caused by tick bites, is a human viral infectious disease involving the central nervous system. The disease is most often manifested as meningitis (inflammation of the membrane that surrounds the brain and spinal cord), encephalitis (inflammation of the brain), or meningoencephalitis (inflammation of both the brain and meninges). TBE cases in Europe have steadily increased over the last few decades. People who live and work or go for vacation/recreational activities into potential tick habitats are at obvious risk of acquiring tick-transmitted infections. These tick bites not only cause infectious diseases and put the public health at risk but also increase the cost of Health Insurance System by further complicating the treatment. For example Germany, alone, spends 26 million euros each year on the analyses of diseases caused by tick bites (Muller, 2012). In this thesis work, textiles decorated with nano-microcapsules encapsulating eucalyptus oil, have been developed and studied for their anti-tick properties to cure and/or prevent the spread of tick-borne diseases.

In order to systematically study the tick repellency through capsules attachment the textile properties were thoroughly studied initially. For the determination of the best suited textile five different textile samples were studied in the first phase. The textiles studied include

i. %100 Carded cotton,
ii. %100 Combed cotton,

iii. %100 Polyester,

iv. %100 Viscose

v. %100 Tencel

Based on the fundamental understanding of the interaction forces it is believed that hydrophobicity helps in enhancing the attachment of capsules to the textile surfaces due to the hydrophobic-hydrophobic interactions. Cotton and polyester, and their blends, were chosen for further study due to their relative higher contact angles of 123.38º $\pm$ 3.91º (cotton) and 121º $\pm$ 5.83º (polyester) indicating hydrophobic nature with DI water after treatment in water repelling finishing solution in addition to their wide availability and use in sports outfits which is also the focus of this project.

In the second phase, for the selection of the most suited cotton, polyester and their blends treated with varying concentrations of silicon in the finishing solution, a design of experiment (DoE) was conducted. The DoE revealed 13 tests to be performed for the design of optimum surface properties to enable maximum nano-microcapsule adherence to the textile surfaces. The responses studied in the DoE include.

i. Change in Weight Per Unit Area (g/m^2)

ii. Contact Angle with DI_Water (Degrees)

iii. Contact Angle with Acacia Oil (Degrees)

iv. Surface Charge (Zeta Potential (mV)) measurements at the pH of finishing solution

v. Surface Charge (Zeta Potential (mV)) measurements at pH of DI Water

vi. Isoelectric Point (IEP)

The optimization of the responses in DoE being focused on higher hydrophobicity and more negative surface charge resulted in highest desirability for

100% cotton fabric treated with higher silicon content in the finishing solution to maximize the capsules attachment. However a blend of %65cotton and %35polyester was chosen which is suitable for the sports outfits, yet it has been prepared with a different weaving style i.e. cotton fibers on top while polyester fibers on the bottom surface. The idea behind this weaving style is that it helps maximize the capsule attachment ability of textile (on cotton side) while reducing the need for ironing (due to polyester fibers) which can deform the nano-microcapsules.

Microcapsules act as small containers of liquids or solids to be released from the inner core under controlled conditions to address a specific purpose. Empty nano-capsules and capsules loaded with eucalyptus oil as the core ingredient were prepared by solvent evaporation technique using diblock co-polymer: polyethylene glycol-polycaprolactone (PEG-b-PCL) as shell material. PEG-b-PCL is biodegradable polymer and has been used for its non-toxic nature, ability of maintaining good mechanical integrity until degraded and being capable of controlled rates of degradation. The developed capsules were characterized based on their surface morphology, size, size distribution, surface charge and controlled release.

Eucalyptus oil was selected among the candidate oils because of EU regulations. Free eucalyptus oil has shown a high antitick efficacy, on human skin, when the treated skin was exposed to the ticks to treated skin and letting them crawl for 5 minutes. However further evaluation of the alternative efficiency test methods is also needed to have a better understanding of tick repellency of eucalyptus oil.

The release of encapsulated eucalyptus oil from the capsules has been studied by change in surface tension after heating the capsules' solutions. The surface tension after the initial heating decreased showing the presence of some free eucalyptus oil (released

from the capsules). After further heating (and then letting the solutions cool) the surface tension was found to increase which can attributed to the lesser amount of eucalyptus oil present in the capsules' solutions.

In the end the selected textile blend was treated, sprayed on cotton side, with the prepared nano-micro capsules loaded with eucalyptus oil. The attachment of capsules to the textile was studied by change in the pre and post spray weight of textile. The capsule attachment results from weight difference are in good agreement with predicted capsules attachment obtained from DoE study for a specific combination of textile composition and the concentration of silicon in the finishing solution. Moreover the presence of capsules on textile surfaces has been verified by SEM analyses.

In summary, an optimal textile composition and weaving style was determined in this study to maximize the capsule attachment ability for tick repellency. It was observed that there is a good correlation between the hydrophobic and electrostatic nature of the capsules and the textile surface.

5.2. Recommendations for Future Work

Eucalyptus oil has been found to exhibit high antitick efficacy, however further evaluation of the alternative antitick/antimicrobial efficiency test methods is suggested in order to have a better understanding of the tick repellency of eucalyptus oil as the results at hand are not sufficient for a clear evaluation of efficacy against ticks.

PEG-b-PCL and melamine based capsules were successfully attached to the selected textile surfaces and it has been suggested that there still room for attaching different other types capsules and their potential applications are yet to be investigated.

The developed capsules have successfully been attached, without using any binder, to the selected textile blend i.e. %65cotton-%35polyester by spraying and dip coating. Further capsules' attachment methods such as attachment during fiber extrusion, padding, screen printing etc. are suggested to be done in order find the most efficient way of attachment of the capsule to the textile surfaces.

The boundaries for the life cycle analysis of the product "TICKOTEX" have been set and a new flow of processes having necessary changes has been proposed, yet the impact of these changes is yet to be studied. Following the finalization of use and properties of all the parameters set for LCA, quantification of LCA and its associated Life Cost Calculation (LCC) has to be performed and has been left as a future work in this thesis.

This work can be extended to other functional textile applications in medical industry since textiles represent a completely perfect interface between medical treatment facilities and man (both patients and employees), explore the possibilities they offer. This work offers potential applications in medical textiles such as

i. Dressings, bandages and antiseptic wound dressings (used for wound healing)
ii. Hygiene, healthcare and protective textiles (to protect against infectious diseases).
iii. Bed sheets of medical facilities (more hydrophobic, antitick and antimicrobial).

APPENDIX A

Conventional process flow along the necessary process changes in manufacturing of the final product.

S. No.	*Conventional processes*	*Process change 1*	*Process change 2*	*Process change 3*	*Process change 4*
1	Desizing				
2	Bleaching				
3	Drying				
4	Singeing				
5	Mercerizing				
6	Rinsing				
7	Drying				
8	Polyester Optical Fixation				
9	Optical Bleaching				
10	Optical Rinsing				
11	Drying				
12	Chemical Finishing	Melamine capsules dip coating: 1. Attachment 2. Waste (caps in Solution)		Melamine capsules dip coating: 1. Attachment 2. Waste (caps in Solution)	Melamine capsules dip coating: 1. Attachment 2. Waste (caps in Solution)
13	Sanforizing		Cyclic capsules spray coating: 1. Attachment 2. Waste (caps in Solution)	Cyclic capsules spray coating: 1. Attachment 2. Waste (caps in Solution)	Cyclic capsules spray coating: 1. Attachment 2. Waste (caps in Solution)
14	Quality Control				
15	Additional Spray				Post Garment Spray: 1. Caps with free E.O. 2. No Waste

APPENDIX B

Interview/survey to assess customer interest for Tick Repellent Protective Textile Materials

1) Greeting and information about interview

Hello, I am X, research assistant at Ozyegin University.

Thank you for agreeing to this interview, which will help the University better understand your needs and preferences regarding pro. Your answers are completely confidential. They will be combined with others to offer a comprehensive study for Tick Repellent Protective Fabrics.

2) Questions regarding fabrics:

First I want to ask you some questions regarding fabric benefits. Feel free to answer as much as you'd like.

a) Which fabrics do you currently use?

b) Why? Which benefits do you like in fabrics?

c) Are you mostly interested in fabrics with better strength, durability, scent, softness,….?

d) What do you not like about currently available fabrics? How can they be improved?

e) Are you interested in fabrics that are multifunctional and protective? Tick Repellent? That will keep away most types of insects; mainly ticks?

3) Questions regarding cleaning fabrics:

Now I want to ask you questions on cleaning fabrics:

a) How do you currently clean fabrics?
b) Do you use conditioner? Why/Why not?
c) Are you interested in detergents that increase fabric benefits? Such as strength, durability, scent, softness, anti-bacteria, insect repellent.
d) Are you interested in conditioners that increase fabric benefits? Such as strength, durability, scent, softness, anti-bacteria, insect repellent.
e) If said yes to either c or d: would you prefer to have this benefit in your detergent or your conditioner?
f) If said no to c and d would you prefer another way of getting the benefit?

A spray?

4) Tick Repellent Concept introduction:

Now I'd like to get your idea about a new product that has just been introduced on the market. It is a fabric chemical that allows protection from insects mainly tick:

"With this new chemical used on fabrics; most of the insects including mainly ticks are kept away up untill 6 months. If washed or exposed to water up untill this time it can be easily replenished"

a) How interested are you in this product on a scale from 0 to 10? -
b) Is there another change you are more interested in? For instance, insect repellent in summer, tick repellent in spring 0 to 10
c) Do you believe a product offering such benefit is valuable to you? 0 to 10
d) Would you buy it? 0 to 10 -

e) Who would you buy it for? (For yourself or for your company?)-

f) Would you be willing to pay 5% more than your current product? 10%? How much more? -

g) How important is the insect repellent benefit to you? 0 to 10 -

h) What would such product need to get bought by you?

i) What may prevent you from buying such product? Please distribute 100 points over below possible concerns

Not enough benefit -

Not sure how to apply it

Not sure about the risks -

Too expensive -

Need to change my routine

Other…..please specify

5) Replenishment Concept introduction:

Now I'd like to go one step further and get your idea about a new product that is being developed. Included in your conditioner, it replenishes the fabric benefit you prefer every time you wash the fabric.

a) How interested are you in this product on a scale from 0 to 10? -

b) Is there another change you are more interested in? For instance, insect repellent in summer, tick repellent in spring? 0-10

c) Do you believe a product offering such benefit is valuable to you? 0 to 10

d) Would you buy it? 0 to 10 -

e) Who would you buy it for?

f) Would you be willing to pay 5% more than your current product? 10%? How much more? -

g) How important is the insect repellent benefit to you? 0 to 10 -

h) What would such product need to get bought by you?

i) What may prevent you from buying such product? Please distribute 100 points over below possible concerns

Not enough benefit -

Not sure how to apply it

Not sure about the risks -

Too expensive -

Need to change my routine

Other…..please specify

6) Conclusion:

Thank you very much for this interview. Is there anything you want to add that we have not talked about?

Thank you,

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