Application of Superomniphobic Finishes on Fabrics for Chemical Protection

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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DECLARATION

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the dissertation is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

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Arsheen Moiz

March 2018

DEDICATION

This dissertation is dedicated to my parents, my husband Moiz Razzaq and my mother in law especially Ghousia Razzaq. Also this dissertation is dedicated to my beloved kids, Wareesha and Aariz for their endless love, caring and support.

Thank you for your encouraging words and limitless faith in my abilities.

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Arsheen Moiz, Rajiv Padhye, Xin Wang. “Coating of TPU-PDMS-TMS on Polycotton Fabrics for Versatile Protection” Polymers.2017; *9*(12), 660, doi: 10.3390/polym9120660

Arsheen Moiz, Rajiv Padhye and Xin Wang “Durable Superomniphobic Surface on Cotton Fabrics via Coating of Silicone Rubber and Fluoropolymers” Coatings. 2018; 8(3), 104, doi: 10.3390/coatings8030104

Conferences

Oral presentation: “Modification of the surface of polycotton fabrics to produce superhydrophobicity” at the Asian Textile Conferences ATC-13 at Deakin University, Geelong from 4-6 November 2015.

Oral presentation: “Protective Cotton Fabric by Coating of Thermoplastic Polyurethane Combined with PDMS-TMS” Proceedings of Fire Resistant Textiles and Fibre Conference TTNA, Melbourne, Australia, 29 November 2016.

LIST OF ABBREVIATIONS AND ACRONYMS

WCA	Water contact angle
CBR	Chemical, biological, radiological
CWA	Chemical Warfare Agent
DS-2	Decontamination solution-2
FAS	Fluorinated alkyl silane
FD-POSS	Fluorinated-decyl polyhedral oligomer silsesquioxane
FTIR	Fourier transform infrared radiation
GSM	Gram per square meter
IEDs	Improvised Explosive Device
IMP	Ion mask technology
ITAP	Improved Toxicological Agent Protective
JSLIST	Joint Service Lightweight Integrated Suit Technology
MOPP	Mission Oriented Protective Posture
NBC	Nuclear biological chemical
OG	Olive Green
PB	Paris blue
PDSM	Polydimethylsiloxane
RB	Royal blue
SCBA	Self-contained breathing apparatus
SG	Safety Gold
STEPO	Toxic Environment Protective Outfit
TAP	Toxicological Agent Protective
TMS	Trimethylated silica
TPU	Thermoplastic polyurethanes
TYVEK	Trade name of polyethylene coated
WOC	Wpu membrane coated with 10% Oleophobol
WPTC	Wpu membrane with 8% PDMS and TMS coated fabric
WPU	Waterborne polyurethane

ABSTRACT

Military personnel on patrol and industrial staff are likely to face various hazards from chemicals that can either kill them outright or cause them serious damage. Chemical substances known as chemical warfare agents (CWA) have been used in war zones since the end of the First World War. These chemical warfare agents are particularly dangerous to human life. They cause skin disease, disability and death of soldiers. These chemicals are also widely used for pharmaceutical purposes, for preparation in industrial plants, in laboratories, in nuclear plants and in food items. However, these chemicals cause toxic effects not only to human life but also to the environment as they have polluted widely including buildings, filtration systems, vehicles and equipment. The chemicals spread easily in the environment and remain for a long time. Finally, CWA was banned from use in 1996, but some of them are still being used in the warzone. Protection of people from exposure to hazardous chemicals, such as chemical warfare agents and toxic or corrosive chemicals is essential in today's battlefield and industries.

Chemical, biological, radiation and nuclear (CBRN) suits are designed for emergency circumstances and are likely to cause a thermal burden when worn over prolonged periods. Special protective clothing is available for use to protect from these chemicals but it is very heavy in weight, uncomfortable and expensive. Exploration of the superomniphobic surface for versatile protection against water, oil, liquids and chemicals has been the key to the development of protective clothing for chemical protection. However, simple, cost-effective methods to develop functional surface on textiles with durability and without compromising comfort much are still of great challenge.

This research aims at developing protective fabrics with a functional coating that is capable of preventing the penetration of water, liquids, oil and certain chemical warfare agents without compromising the fabric weight and comfort properties. The intention of this research is not to develop a replacement for CBRN suits but to develop low-level threat fabrics that can either be used as combat uniforms and selective parts of the uniform or be applied in industrial protection. A widely used coating method of padding-knife coating-padding-curing was employed in this research to perform functional coating on fabrics towards high-performance protective clothing. Polymeric coating of polyurethane or silicone rubber membrane in combination with repellents including polydimethylsiloxane (PDMS), trimethylated silica (TMS) and fluoro-polymers was developed to form superomniphobic surface on cotton and polycotton fabrics, and a comparison with coated fabrics with plasma treated fabrics and industrial fabrics was performed to justify the developed technology from this research. The coated fabrics were characterised by thickness, morphology and chemical components to understand the structure and mechanism of the coating. Measurements of protection against water, oil, aqueous liquids and chemicals and hydrostatic pressure were performed to test the versatile protection of the coated fabrics. Besides, the air permeability, water vapour permeability, thermal resistance, handle, stiffness and moisture management properties were tested to study of the comfort of the coated fabrics.

It was found that the combination of polyurethane membrane and PDMS-TMS acted as repellents to give better results in terms of protection against water, liquids, oil, chemical, hydrostatic pressure on the fabric surface. The developed surface presented hydrophobicity with a water contact angle of around 150^{o}, and the droplets of water, oil, aqueous liquids and chemicals were repelled for long periods. A cross-linked network was formed between the membrane and the PDMS-TMS, resulted in the excellent durability of the coating against different cycles of laundering and crocking together with rubbing. The comfort of the coated fabrics was compromised due to the blocking of the porous structure of the fabrics, but the selection of the coated membrane such as the thermoplastic polyurethane would improve the comfort to some extent. The coated fabrics were comparable to the plasma treated fabrics for defence and industrial fabrics in terms of protection and the coated fabrics can withstand much higher hydrostatic pressure than the other two. The advent of high-performance coating was suitable for long time protection for chemical as well as comfortable properties for the protective clothing for military and industry.

1 INTRODUCTION

1.1 Background

Chemicals are dangerous to human as they can enter human body to create severe diseases on the skin, causing disability and in some cases death within seconds (Russell et al., 2003). Chemical warfare agents (CWA) together with other toxic and corrosive chemicals in different industries and laboratories can cause skin disease, disability and death of soldiers and related personnel (Truong et al., 2008). It is thus important to provide better protection against these chemicals and to control their harmful effects to the human life. Protective clothing and related equipment are playing a key role in covering the whole body and providing an excellent barrier to these chemicals exposures (Rimpel, 2008). Chemical, biological, radiation and nuclear (CBRN) suits were developed for the protection purpose, and Fluorine based compounds were widely used for creating superhydrophobic surfaces for protective clothing (Schultze P-E, 2006). Research efforts have contributed to the surface science in terms of chemical protection. With the advanced materials being employed and novel fabrication techniques being developed, protective clothing with superomniphobic surface and versatile protection capacity has been developed (Moiz et al., 2016).

However, traditional protective clothing is heavy, bulky, inflexible and uncomfortable, and all the protective clothing provides limited protection against chemicals due to the imperfection of natural or synthetic fibrous materials available today (Sawhney et al., 2008). Fluoro-based compounds may cause environmental issues in the usage of the developed products (Hekster et al., 2002). Superomniphobic surface, namely surface that displays a contact angle of $>150^o$ along with low contact angle hysteresis with essentially all high and low surface tension liquids, including water, oils and chemicals, is necessary for developing protective clothing (OTA, 2014).

A simple and cost-effective technology to develop superomniphobic surface from new polymer materials with durability and without compromising the comfort is still of great challenge.

1.2 Research question

The research question of this PhD work is: how to develop a durable superomniphobic coating on fabrics effective as chemical, oil and liquid/water resistance and comfortable in real service, achieved from environmental friendly materials and by using the simple and cost-effective method. More specific research questions are as follows:

1. How can superomniphobic surface help to enhance the resistance against chemicals, oil and liquids/water on fabrics?
2. What is the mechanism of crosslinking between the coated layers and fabrics that endows the durability of coating?
3. How does the pad-knife-pad-cure method enhance the chemical protection while maintaining the comfort level?
4. How to make the critical comparison between the developed protective clothing with the industrial and plasma treated fabrics?

1.3 Aim and objectives

The aim of this research is to develop a simple and cost-effective coating technology for creating a durable superomniphobic surface on fabrics, targeting at providing low-level protection support against water, aqueous liquids, oil, chemicals and hydrostatic pressure while maintaining fabric comfort.

The objective of this study is to coat polyurethane or silicone rubber membrane in combination with polydimethylsiloxane (PDMS) and trimethylated silica (TMS) and other repellents. The objectives of this research are:

- To study and understand chemical protection mechanism and the current technology to develop protective clothing in this regard. A thorough understanding of the hazards and risks associated with chemicals will be contributed and current development of protective clothing will be studied to better understand the context of this research and help select the proper materials and formulate applicable techniques.
- To investigate the application of layer-by-layer coating technique to form functional layer on fabrics from polyurethane and PDMS-TMS. The effect of experimental

details on the properties of the as-coated fabrics will be assessed to develop the trustable and effective coating technique.

- To characterise the developed fabrics in terms of structure and properties, protection and comfort. A reproducible technology will be contributed with the high protective fabrics developed for further application in clothing upon the support of the results and outcomes in the research.
- To understand the cross-linking mechanism between the coated layers and study the durability of the coating. This will help justify the developed technology in terms of coating durability and application potentials.
- To make a critical comparison of the developed fabrics with plasma treated fabrics and industrial fabrics. The protection, comfort and the associated techniques will be compared and help develop the most robust, simple, trustable and effective technology in developing protective clothing for chemical protection.

1.4 Significance of research

The developed technology can be adopted for many applications in the textile industry. The pad-knife-cure coating method is a simple method, useful for large scale in the textile industry to develop low-level protective clothing for military garments. The polymeric coating with repellent is useful for commercial garments such as lab coats, rain coats, protective jackets, gloves, boots and protective suits. This research provides better protection to water, oil, chemicals and a strong barrier for severe skin diseases. People working in chemical environments such as industrial plants for manufacturing and production units for chemicals use protective suits or lab coats, goggles, gloves and boots to provide better protection for oil and water but not for chemicals. Scientists working in a laboratory wear cotton lab coats. However, cotton has wettability properties and it can be easily absorbed many types of chemicals resulting in direct skin contact and potentially creating a rash or infection on the body.

The low-level protective fabrics would be applicable as military garments or industrial protection gears and provide better protection for hazardous chemical, skin diseases, disability and deaths. The new innovation of superomniphobic surface with simple and commonly feasible techniques can be applicable for hydrophobic coating, waterproofing and semipermeable membrane in many industries. This newly developed protective fabric can successfully commercialised because it provides not only a chemical protection but also resistant to soil, stain, oil and water.

Theoretical perspectives are important because they provide the assumption or ideas to develop a new theory to explain the new framework, information and issues with bonding between substrate, membrane and repellents. The experimental work/observations and results give a new practical approach and methodology to achieve more beneficial work for research.

This research has greater significance for industrial purposes because it represents a novel, feasible process for the large production of fabrication in the textile industry. Protective clothes are useful for chemical protection, comfort, lightweight and cost for military combat uniform and civilian garments.

1.5 Dissertation overview

This dissertation consists of eight Chapters as overviewed below.

Chapter 1 consists of the basic information about the nature of research exploration, the aim and objects, the methodology, and the significance of the proposed research.

Chapter 2 presents an intensive literature review to understand different aspects of the research problems. The classification of chemical warfare agents, chemicals with different level of hazards, chemical protection materials and techniques together with the mechanism and application of superhydrophobic surface were carefully reviewed and discussed.

Chapter 3 provides details of the experimental work, including the materials and chemicals used, methods adopted, and details of the measurements and characterisation for investigating the structure and physical properties, protection and comfort of fabrics.

Chapter 4 focuses on the development of multiple protective cotton fabrics from waterborne polyurethane in combination with PDMS and TMS by the pad-knife-pad coating method. The mechanism of the coating together with the results and discussion in the characterisation, protection and comfort of the coated fabrics will be delivered in details.

Chapter 5 details the layer-by-layer coating of thermoplastic polyurethane in combination with PDMS and TMS on polycotton fabrics. This chapter investigates the effects of TPU polymeric coating on the comfort and moisture management together with handle properties of the fabrics, based on the overall study on the versatile protection of coated fabrics.

Chapter 6 details the development of silicone rubber membrane in combination with fluoro-polymers for the superomniphobic surface. The protection and comfort of the coated fabrics are presented and discussed in details.

Chapter 7 presents a critical comparison of the coated fabrics with plasma treated fabrics in defence and industrial fabrics. The structure and morphology, protection and comfort of all the fabrics are compared to justify the developed coating technology in this research.

Chapter 8 outlines the conclusions that have been drawn from this research. The scope and limitations are listed and the recommendations for future research are made to guide further endeavour.

2 THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

Protective clothing is essential for military force and civilians, and its purpose is to provide better protection against the hazardous chemicals in the war zone and environment. Chemicals are dangerous to human as they can enter human body to create severe diseases on the skin, causing disability and in some cases death within seconds (Russell et al., 2003). It is thus important to provide better protection against these chemicals and to control their harmful effects to the human life. Protective clothing and related equipment are playing a key role in covering the whole body and providing an excellent barrier to these chemicals exposures. For instance, chemical, biological and radiological (CBR) suits have been developed to provide the better protection in specific areas (Thakare et al., 2017). Traditional protective clothing is heavy, bulky, inflexible and uncomfortable, and all the protective clothing provides limited protection against chemicals due to the imperfection of natural or synthetic fibrous materials available today. Advanced technologies of protective clothing consist of multi-layer fabrics have been developed to provide high-performance protection towards versatile applications such as Joint Service Lightweight Integrated Suit Technology (JLIST), Mission Oriented Protective Posture (MOPP) and Polytetrafluoroethylene (PTFE) membrane (Turaga et al., 2012). Current technologies in this area aim to reduce the number of layers while enhancing the comfort level and strengthen chemical protection (Truong et al., 2008).

2.2 Chemical protection

Chemical substances can enter the human body through its digestive system, by inhalation and/or absorption through the skin.

Chemical protection is required for specific areas such as the plants where these chemicals are being manufactured, handling of pharmaceuticals, pesticides, insecticides, and herbicides, laboratories and electronic industries.

Chemical protection is required at two different levels. The minimum hazardous chemicals are used for decontamination in industry, laboratory, nuclear plants (radioactive dust particles), such as concentrated liquids immersion or splash and vapour. Staff handling these chemicals must be protected by wearing filter masks, protective suits or lab coats and gloves to avoid direct contact. For handling minimum hazardous chemicals used in hospitals (e. g. for X-ray) and welding, gardening and road work, personnel are required to wear an apron, fluorescent jacket, goggles and gloves (Truong et al., 2008).

Hazardous chemicals are widely used for storage, manufacturing, packing, production, decontamination and warzones (Russell et al., 2003). Related personnel must be covered with full protective mask, suits, and gloves and over boots (O’HERN et al., 1917). For other hazardous chemicals that are not absorbed by the skin but are highly toxic through inhalation, the staff must use breathing apparatus for completely sealing out chemical vapours (Turaga et al., 2012).

2.3 Chemical warfare agents

Chemical warfare agents (CWA) are those substances used in the war zone to destroy the lives of soldiers and civilians. These chemical substances have been very effective in causing death, disability and severe skin diseases. Table 2-1shows the brief history of chemical warfare agents. At present, the only way to protect human from CWA is using special CBR suits and face masks and decontamination solution-2 (DS-2) for the skin. The DS-2 solution contains 2% sodium hydroxide and ethylene ether that can neutralize all the toxic chemicals agents (Rimpel, 2008). CWA not only destroy human life, but also damage the building, filtration units, vehicles and equipment etc. Coating with different polymers and CBR protective suits are thus necessary for decontamination purpose (Russell et al., 2003).

Table 2-1: History of chemical warfare agents (Truong et al., 2008).

Year	Chemical Warfare Agents	Location
1914	Chlorine, Chloropicrin, Phosgene & Mustard gas	London, France
1919	Arsenic gas	Russia
1920	Chlorine gas	Mesopotamia
1920-1927	Sulphur Mustard gas	Berber rebellion
1930-1936	G-series & Sulphur mustard gas	Ethiopia
1939-40	G-series & Nerve agents (developing chemical and biological weapons)	Yemen
1944	Sulphur mustard gas	London
1950	134 (New test methods of Chemical, Biological and Radiological agents) New class of V-series (1961)	
1960	Egypt	Eritrean rebels
1970	Ethiopia	Laos
1975-81	Multiple chemical warfare agents	Kampuchea
1979	Lewisite (Blister agents)	China
1980	Choking agents and Nerve agents	Afghanistan
1983-87	Sulphur Mustard gas	Iran
1988	Chlorine gas chambers	Iraq (Halabja)
1994	Sarin gas	Japan ((Matsumoto)
1995	Mustard gas	Tokyo
1996	Chlorine gas	Japanese(underground rail station)
1997	Banned of chemical warfare agents	
2001	Conventional (missile) Aircraft	World Trade Centre, New York-USA
2001	Conventional (explosive) planted Bomb	United states America
2002	Multiple no of chemical warfare agents	Moscow
2004	Conventional (explosive) Planted Bombs	Madrid Commuter Trains
2005	Chemical (Chlorine with Vehicle-borne (explosive)	London Underground
2006	Conventional (explosive)Planted Bombers	Iraq
2006	Conventional (explosive)	Mumbai Commuter Trains
2010	Conventional (explosive) Suicide Bombers	Moscow Subway System
2014	Conventional (explosive) Suicide Bombers	Pakistan
2015	Conventional (explosive) Suicide Bombers	Afghanistan
2016	Chemical Weapons	Syria
2017	Chemical Weapons attacks (missiles)	Syria

Awareness of the risks of CWA is a very important factor for controlling their effects and for protection. These chemical warfare agents are divided into five classifications according to the nature of structure, effect and mode of exposure.

2.4 Classification of chemical warfare agents

2.4.1 Blister/Vesicant agents

Blister agents, as the name indicates, are those produce the blisters on the skin. These agents are harmful and produce skin diseases in war zones, with the names of sulphur mustard (HD), nitrogen mustard (NH_1, NH_2 and NH_3) and lewisite (L).

Sulphur mustard is also known as Mustard gas (HD) which persists for one day in summer and four days in winter. It can easily penetrate ordinary clothing in the vapour form, and it is the most widely used gas in war zones that affect skin, eyes and lungs. Protection gears against sulphur mustard gas can be protective masks and gas filters, and protective suits and decontamination wipes are also effective (Russell et al., 2003).

Nitrogen mustard (NH_1, NH_2 and NH_3) is available in liquid form. NH_3 is normally used in war zones which persist for only 10-15 minutes, and it can easily penetrate ordinary clothing in vapour form. It affects skin, eyes, respiratory tract and gastrointestinal tract, and it is also effective on the central nervous system and bone marrow suppression. It can be protected by a gas filter, mask and protective suits (Gorzkowska-Sobas, 2013).

Lewisite (L) exists only in liquid form, and it persists in summer for one hour and one day in winter. Lewisite is regarded as a more toxic chemical to destroy human life, as it can easily penetrate ordinary clothing and even rubber materials, and protective suits are not effective to it.

2.4.2 Nerve agents

Nerve agents are more power CWA. Two groups of nerve agents are identified due to their chemical compositions, namely the G-agents (fluorine- or cyanide-containing organophosphates) and the V-agents (sulphur containing organophosphate) (Russell et al., 2003). The names of nerve G-agents include Tabun (GA), Sarin (GB) and Soman (GD), with the letter ‘G’ represents Germany as the country of origin. The chemical names of them are Ethyl N, N′-dimethyl phosphor amidecyanidate (TABUN) for GA, Isopropyl methyl phosphono fluoridate (SARIN) for GB and Pinacolyl methyl phosphine fluoridate (SOMAN) for GD, respectively. Another class of nerve agents is V-series with the letter ‘V’ stands for “Venomous”. V series was introduced in 1961. The name of V-series chemical warfare agents is Vx, and the chemical name is o-ethyl S-2 di-isopropylaminoethylmethyl phosphonothioate.

G-series are present in liquid form, and these chemicals persist in summer for one day and winter for four days. These powerful chemical warfare agents can destroy human life in 10-15 minutes.

Nerve agents affect the central nervous system, which is why the agents are called Nerve agents. Besides, the Verve agents affect eyes, lungs, skin and nervous system, causing the blood preventing oxygen from reaching body tissues. The protection against Nerve agents includes masks and gas filters, and protective suits and decontamination wipes. Cyclosarin (GE) can penetrate the skin and be inhaled through the respiratory tract. Vx has simpler property as G-series. It persists for three days in summer and eight days for winter. Protective suits, masks and gas filters, and documentation wipes for skin irritants are used for the purpose of protection.

2.4.3 Choking agents

The chocking agents include chlorine (CL), phosgene (CG) and diphosgene (DP). Chlorine and phosgene are available in the gas form, while diphosgene is available in liquid form. The choking agents can result in chest tightness, breathlessness, acute lung injury, burning sensation in the nose, throat and eyes, and redness and blisters on the skin. These agents can be protected by wearing protective suits, protective masks and a gas filter. However, chloropicrin can penetrate gas mask filters and cause vomiting.

2.4.4 Asphyxiants/Blood agents

Blood agents can block the oxygen in blood cells, producing the poisoning enzyme cytochrome oxidase which causes body dysfunction. Asphyxiation would usually occur and for this reason, the chemical warfare is called Asphyxiants agents. The names of Blood agents include Hydrogen cyanide (AC), Cyanogen Chloride (CK) and Arsine (SA). Arsine is known as a low toxicity chemical warfare agent. The cyanide compounds are effective in chemical asphyxiates because the cyanides interfere with oxygen transport at the cellular level and this causes tissue hypoxia, anaerobic metabolism and lactic acidosis. Cyanogen causes breathlessness, headache, dizziness, anxiety, palpitations, mydriasis, blurring of vision, nausea and drowsiness. Arsenic gas inhaled in the body causes rapid destruction of red blood cells, leading to hypoxia and renal failure. The blood agents can easily enter the skin, so that protection against these agents is mainly by wearing protective suits, masks and gas filters.

2.4.5 Behaviour agents/Vomiting agents

The names of behaviour agents are Adamsite (DM), Diphenylcyanoarsin (DA) and Diphenylchlore (DC). These agents persist in aerosol form (long or short solid state) and affect the central nervous system, eye, heart, respiratory system, skin, gastrointestinal tract and urinary bladder. Behaviour agents can easily penetrate the skin and produce severe skin diseases in human life (Russell et al., 2003), so that the protection against these agents is by using protective suits, mask and gas filter masks.

2.5 Chemicals used in war zones for chemical resistance analysis

The stimulant compounds are those compounds which have relevant chemical and physical properties of chemical warfare agents, without producing any toxicity for the environment and human life. In other words, these compounds are used for research activity to ensure safety. The purpose of stimulant/alternate chemical warfare agents is to use an ideal compound to predict chemical exposure, persistence, and to formulate disposal strategies and to control contamination.

The persistent chemical warfare agents' means the agents present in the air for 24 hours, and non-persistent chemical warfare agents mean those for 10-15 minutes (Gorzkowska-Sobas, 2013). Toxic chemical warfare agents are restricted to use in the research laboratory because there are very toxic in nature and not feasible to use in the safety precaution of the laboratory. The research work has to be done by using the alternative compounds of CWA to provide the protection in the war zone and to overcome the causalities and disability of human life (Chilcott, 2014).

The alternative compounds of sulphur mustard (HD) are methyl salicylate (MS), Chloroethyl phenyl sulphide (CEPS), Dimethyl adipate (DMA) and Chloroethyl ethyl sulphide (CEES/HM). GA is simulated by Di-isopropyl fluorophosphates (DFP), Diethyl ester phosphonic acid (DEEP), Diethyl malonate (DEM), and Diethyl ester phosphonic acid (DEP). Alternative compounds for GB include Bush, 1 Butanethiol (DMMP), Dimethylmethylphosphonate (DPGME), Dipropylene glycolmonomethylether and Ethanol. GD alternative compounds are Ethylchloroacetate (ECA), Triethylphosphate (TEP), Trimethylphosphate (TMP), Diethylethyoxyphosphate (DEEP), Di-phenylchlorophosphate (DPCP). Alternative compounds for VX are bis (2-ethylhexyl) phthalate, Diethyl sebacate (DES), diethyl phenyl phosphonothioate (DEPPT), and Parathion and ambition. Lewisite is used as alternative compounds in the form of Lewisite oxides and Phenyl arsine oxides. These alternative compounds were used for research activity, such as decontamination by hydrolysis, neutralisation with peroxides, oxidation of bleaches and other related reagents, detoxication with acid and basic media, and metal catalysed reaction (Wagner et al., 1999, Bartelt-Hunt et al., 2008, Kim et al., 2011).

2.6 Lower and higher level protective suits

Toxicological Agent Protective (TAP) polyethylene coated suits (TYVEK), including adjustable collar, double sleeves, trouser cuffs, belt and mask, are widely used for liquid splash protection for one hour. There are protective suits for police and other civilians like yellow and orange fluorescent dyed suits. The air permeable or breathable suits such as Rampart, Saratoga Hammer (Truong et al., 2008, Turaga et al., 2012) and Tychem, and Kapplers commander brigade impermeable suits are commercially available for low-level chemical protection. Toxic Environment Protective Outfit (TEPO) also produces protective garments for civilians (Turaga et al., 2012).

In the past, different substances were used for skin protection, such as resin oils and charcoal coated suits. Chemical warfare agents (CWA) then became the major threats on the battlefield. CWA was available in solids, liquids and gas forms, in which the solid ones were easily spreading by the wind, liquids were easily penetrating the skin and gases were unhealed into the respiratory tract. These chemical substances were the cause of 99% of deaths and skin diseases and 80% of disability. In the initial stage, some butyl rubber suits were used to protect against these chemical warfare agents but the CWA Lewisite easily penetrated butyl rubber (Russell et al., 2003). Besides, butyl rubber was not comfortable to wear due to its low breathability. The charcoal coated suits did not work against chemical substances because all substances were easily absorbed (Cowsar, 1980, Glitz et al., 1994). In the 1970s, protective suits were developed using PU foam coating to resist chemicals, but it did not work properly because mustard gas penetrated into the foam and the fabrics (Kovačević et al., 2010).

In 1993, JSLIST of USA made special protective suits knew as CBR suits. There were five multilayer carbon active suits (Rimpel, 2008). This provided protection against wind, rain, air born virus, liquids chemical and bacterial. With its weight of about 5-7 lb, the suit contained 50% cotton and poplin and 50% nylon. JLIST developed a range of protective suits including helmets, gloves, masks, footwear and bodysuits with a cooling system for special condition of 24 hours in the war zone. Mission Oriented Protective Posture Gear (MOPP) designed CBR protective suits with four levels of protection. MOPP Level 1 and 2 did not provide the complete protection for more than two hours. But MOPP level 3 and 4 provided complete protection for more than six hours, including suits with mask and gloves carried (Rimpekl et al. 2008). French Paul Boy’s (NBC) developed the carbon base air permeable combat uniform suits. Chemical protective suits of USA exhibited vapour protection for 12 hours (Boopathi et al., 2008, Truong et al., 2008). Gore-Tex fabrics are water resistant, wind proof, washable and breathable, but the fabrics are not suitable for chemical protection. Improved Toxicological Agent Protective Ensemble Gloves and Boots (ITAP) or Breathable Apparatus (SCBA) is used in emergency condition for fire-fighters. Kappler response fabrics are useful for chemical protection. Toxic Environment Protective Outfit (STEPO) or suits with breathable apparatus are used for civilian emergency conditions to withstand chemical and biological agents, missile/rocket fuels, petroleum oils and lubricants (POL) and industrial chemicals.

There have been other advances in technology like carbon nanotubes, selectively permeable, impermeable and self-cleaning materials to make protective garments against CWA (Truong et al., 2008).

2.7 Chemical protection by Fluoro-compounds

Fluoro-compounds depend upon the strength of bonding between carbon and fluorine atoms. Fluorinated-compounds have the unique property to react as a single molecule with copolymers and homopolymeric substances for a variety of applications. Fifty years ago, it was introduced into the market and was used as a covering on products all over the world. Fluorinated-compound has been widely used on paper, paperboard, leather, carpet, textile, fire extinguishing equipment and surfactants, cooking (non-stick pans) etc. Fluoro-surfactant was also used for laundering of garments. The Fluoro-compounds were used as protective clothing (raincoat, rain proof jackets, and boots) (Schultze P-E, 2006). In the textile industry, fabrics coated with Fluoro-compounds provided resistance to stain, soil, oil, and also water repellency. Between 1998 and 2000, there was a great deal of activity in research laboratories, regulatory authorities and industry to classify, monitor and regulate these pollutants (Hekster et al., 2002). These Fluoro-compounds were very harmful to health and environment. Fluoro-compounds like perfluoro-carbons (PFCs) and sulphur hexafluoride (SF_6) were measurable in the environment and impacted on climate condition. These compounds were quickly destroying the ozone layer and creating greenhouse gas. In 2005, Paulsen reported the telomere (FTOH) compounds which were used in the paper and boards industry to provide protection against grease and water (Poulsen, 2005). These compounds were treated in food contact items (cooking pans, disposable plates, food container, warping paper or bags) and non-food items (folding cartons, carbonless forms, masking paper and tapes) (Santillo, 2006).

Fluoro-compounds breakup easily (hexafluoro-propylene and perfluoro-isobutylene) and can enter food and non-food items (reported by Waritz in 1975) (Hekster et al. 2002). The analysis methods of toxic fluoro-polymers (PTFE) in cooking pans is described by Ellis (Ellis, 2001). The fluoro-polymers broke up into different compounds and penetrated into foods. Boulanger and Butenhoff also reported that fluoro-compounds in detergents, repellents, waterproofing, raincoats and protective garments broke up and penetrated into the skin and the human body (Boulanger, 2005, Butenhoff, 2006). Many companies, including Clariant, Bayer, Ciba, Daikin and DuPont, provided fluoro-compounds and claimed that these compounds were stable and strong bonding with other compounds (Santillo, 2006). However, wrong information about these compounds and they were already being found in textile wastes.

Dinglasan Panlilio and Mabury (2006) reported that the fluoro-compounds of telomere methacrylate (FTOH) were also present in sewage water (Dinglasan-Panlilio, 2006). Two compounds, perfluoro-octane sulphonate (PFOS) and Perfluoro-octanoic acid (PFOA), represented in biological samples, showing degradation in human blood serum levels between 17-53 µg /L for PFOS and 3-17 µg/L for PFOA. No differences could be observed between children with 37.5 µg/L and elderly people with 31µg/L. These fluoro-compounds were also persistent in the environment for many years (Hekster et al., 2002).

The research done between 1998 and 2000 monitored the effects of fluoro-compound in the world. The organic pollutant compounds were then banned because of their persistence and harm to the health of wildlife, sea life and human life. In the United Kingdom and Sweden, the use of flour-compounds was restricted in different on-going projects and a specific application deadline was announced from 2007 to 2010. Concerning for the environment and human health, USA and China also announced an international ban on these compounds in 2013 (Butenhoff, 2006, Santillo, 2006).

2.8 Chemical protection by Polyurethane

PU is a useful polymer that is environmentally friendly and is widely used in textiles. PU has unique properties to provide many applications without any harmful effects to human life. PU does not produce any skin allergy or disease. Textiles coating plays an important role in the textile industry for different protection and functions, and PU coating has been used as hydrophobic materials in many applications due to their relatively safe nature when compared to fluoro-based polymers (MacPhee and Barton, 1987). The origin of polyurethane (PU) dates back to the beginning of World War II. It was first developed as a replacement for rubber to be used as coating materials.

PU coatings were used for the lamination of paper, the manufacture of mustard gas resistant garments, high-gloss aeroplane finishes and chemical and corrosion-resistant coatings (Kovačević et al., 2010).

In 1970, Department of US Army required the application of chemical agent resistance coating (CARC) and thus PU painting was used in military equipment such as combat support, tactical wheeled vehicles, aircraft, and essential ground support (Duncan et al., 2001). TPU elastomeric based materials are suitable for protective clothing such as face masks, which resists chemical warfare agents (CWA) with desirable physical properties (Scott, 2005). PU coating was used as a peel-able coating to absorb the chemical warfare agent on the surface of military equipment.

Polyester base polyurethane (PUS) was used as the direct coating for rainproof garments, due to its thermoplastic nature in fabric coating (Crawford and Escarsega, 2000). PU waterborne dispersion coating was also used in military equipment (Fricke et al). Water-dispersible PU coatings were used for the coating of exposed equipment such as military tank and other vehicles. PU was used as paint coating to oxidation to decontaminate chemical warfare agent on military vehicles (Gheewala and Wytiaz, 2003). PU coatings were applied on fabrics to produce shape memory and air permeable fabrics (Cho et al., 2004). PU was also used to enhance the mechanical properties and the flexibility of fabrics (Walker et al., 2003).

PU used as microporous membranes with the self-decontaminating agent (polyoxometalate) were used to form a film for decontamination of the G-agent and HD surrogates on fabric surface (McPherson, 2005). PU laminated coating was combined with polytetrafluoroethylene (PTFE) laminated microporous membrane to produce water and vapour resistant fabrics in sports textiles industry (Jayaraman et al., 2006). Waterproof-breathable PU coating has been used as a unique layer with nanostructure in the protective clothing and sportswear industry (Kang et al., 2007). Electrospun nanofibre web provides good moisture, hydrostatic stability to water, self-cleaning property, drug delivery and vapour release properties while maintaining water and wind resistance. PU has been used effectively in textile coatings for garments, such as raincoats and industrial safety clothing against various hazards. Thermoplastic polyether-based PU is resistant to various micro-organisms and bears exceptional hydrolytic stability in fabrics (Cha et al., 2006, Fan and Chen, 2002).

PU nanofibres were used as the high-performance barrier for breathable and waterproof clothing, and as thermal comfort materials of protective clothing (Romaškevič et al., 2006). PU-based materials were used for immobilization of enzymes and cells in biological and medical fields, such as biocompatibility and stability of water, drug delivery and medical devices (Russell et al.

2003). PU has been used as biocide materials to prevent the enzymatic attacks and to provide antibacterial properties on the fabric surface and paper (Boopathi et al., 2008, Makal et al., 2006). PU has been used as a protective membrane with nanoparticles to provide protection against pesticides, organic volatile solvents and other liquids chemical warfare agents. PU has also been used as the selective semipermeable nonporous membrane in protective clothing (Scholten, 2011). PU has been combined with silica nanoparticles and fluorinated polymer to develop superomniphobic breathable membranes for oil resistance (Wang et al., 2012). PU coating with an ammonium salt and other polymer were used as single or multi-functional materials to decontaminate chemical and biological warfare agents. Microporous PU membranes exhibited robust mechanical property with good air permeability, high water resistance, water vapour transmittance and comparable tensile strength as a significant result of one step methods (Turaga et al., 2012).

PU coating was used as multi-functional, self-decontaminating materials to remove the gram positive and negative bacteria as well as biological chemical warfare agents. PU coating was also used as the peel-able coating to absorb the chemical warfare agent on the surface of military equipment (Gazi and Mitchell, 2012). PU and fluorinated polymer were combined together to produce the microporous membrane to improve the breathability, air permeability, weather resistance, water vapour transmittance and tensile strength property of fabrics (Schutzius et al., 2011). This work also provided a versatile strategy for further design and development of PU membranes on a large scale towards various applications (Kovačević et al., 2010). PU was also combined with silver and titanium dioxide nanoparticles by electrospinning and electrospraying to produce protective membrane against the attack of chemical warfare agents (Ryu et al., 2013). Polyurethane was mainly used with nanoparticles and fluoro-polymer as the microporous, semipermeable and breathable membrane for the chemical protection (Li, 2017).

2.9 Chemical protection by nanocoating

Nanotechnology focuses on the development of nanomaterial, nanostructure and nanoparticles with various applications in the fields of science, engineer, plastic, aerospace, medical, electronic and smart and intelligent textiles (Joshi and Bhattacharyya, 2011). Multi-function is introduced to enhance the properties of products for a wider range of application and in the textile industry, nanotechnology was adopted to enhance the multi-functional properties of fabrics (Brzeziński et al., 2009). Nanofibres, nanofinishes, nanocomposite and nanocoating has seen applications to endow the surface modification, water, oil repellency, ultraviolet (UV) radiation, hydrophobicity, military protection, medical and self-cleaning properties of fabrics (Joshi and Bhattacharyya, 2011). Nanocomposite fibres that consist of nanoparticles have improved the temperature resistance, dye-ability, mechanical and thermal stability, antibacterial and non-flammable properties of textile materials (Hebeish et al., 2013). The nanocoating was also used to refine the coating and finishing of products including medical, optical and electrical devices.

Nanocomposite fibres refer to three types of fibres containing nanofiller, nanoclay and nanotubes (CNT), respectively. Electrospinning and electrospray techniques were usually used to the nanocomposite fibres. The nanofiller were used as multiple layers of silicate or nanoclay. Carbon nanotubes were used to generate hybrid nanostructures as reported (Ramaseshan and 2007). The carbon nanotubes were usually combined with metal oxide nanoparticles including TiO_2, ZnO, Al_2O_3 and SiO_2 (Martin et al., 2005). Nanoclay fibres were combined with maleic anhydride to improve the dye-ability of polypropylene, and the tensile strength, thermal stability, dynamic and creep of the nanocomposite filaments were improved at the same time. Nanofiller and polyhedral oligomeric silsesquioxane (POSS) hybrid with graphene oxide to increase the thermal resistance of multiple application (Xue, 2012). Nanoclay was added into polyurethane to improve the thermal stability, flame resistance and dye-ability, shrinkage and control of swelling of textiles. Polyurethane combined with clay were also applied to nylon substrate to improve the gas and water protection, tensile strength, heat and weather resistance (Joshi and Bhattacharyya, 2011). Novel polyurethane hybrids with nanographite particles or with metal oxides such as iron and nickel were used in defence as camouflage coating for the filtration system, vehicles, equipment and building (Truong et al., 2008). Polyurethane was combined with metal oxide nanoparticles to enhance the durability, flexibility and microwave shielding effect and self-decontamination of the coating (Wynne, 2011).

2.10 Superhydrophobic surface

The textile industry has made many advances in the use of technology to improve the surface properties of fabrics, such as the protection against liquids including water, oil, stain resistance, water proofing, breathability, fire protection and greater comfort. A superhydrophobic surface is the key to surface functionalisation of textiles. A hydrophobic surface on textiles provides good resistance to water, oil and soil. Superhydrophobic surfaces are created artificially using nanomaterial, fluoro-carbon polymers and waxy materials to increase the surface roughness of the substrate while decreasing the surface energy (Luo and Huang, 2014). Fluoro-carbon compounds have also been used to provide better resistance to oil and water via a superhydrophobic surface on the surface of textiles. Naturally occurring superhydrophobic surfaces are widely available in biological science.

Butterfly wings, legs, water spiders, geckos' feet and some plant leaves are examples of the superhydrophobic and self-cleaning surface (Chinchwade et al., 2014). The term superhydrophobic is defined as repellence to water droplets, or resistance to water, or water droplet rolling off.

Materials are used to reduce the adhesive property and air gap between the solid state and surface particles. A superhydrophobic surface has the property to control water molecules outside the fabrics and does not allow water to penetrate the fabrics with non-wettability. A hydrophobic surface has endowed different surface morphology and surface tension to fabrics with reduced surface energy. It has the key factors involved to reduce the surface energy and to increase the surface roughness of fabrics. The superhydrophobic surface is determined by the water contact angle (WCA) measurement of >150° (He et al., 2004).

A superhydrophobic surface has the unique property to repel dirt particles, soil, oil, stains and water molecules. The hydrophobic, anticorrosion, anti-fog and self-cleaning properties are endowed by the superhydrophobic surface for applications such as painting, sports, protective and outdoor clothing, integrated sensors, micro fluids and biomedical layers (Liu et al., 2010).

Fluoro-polymers were banned all over the world due to the toxicity involved. A perfluoro-alkyl chain C_6 was used as a replacement for fluoro-compounds to solve the environment and health issues. Paulsen and Jensen (2005) discussed the possible alternatives to fluoro-compounds such as perfluoro-butane sulfonate (PFBS) or C_4, CF_3 or C_2F_5 pendant fluoro-alkyl polyether, dodecafluoro-2-methylpentan-3-one (CF_3-CF_2-CO-CF-$(CF_3)_2$) and C_6 and sulfosuccinate and compound, and these alternatives were found to be useful for paint and wetting, as dispersing agent and in coating industry. Silicone polymers such as fluorinated alkyl silane (FAS), fluorinated-decyl polyhedral oligomeric silsesquioxane (FD-POSS) and dodecafluoro-heptylmethacrylate (DFM) are also useful for non-wetting, painting and ink industry (Poulsen, 2005).

Silicone polymers are also used as the alternate compounds in the textile industry to produce a superhydrophobic surface on fabrics. Silicone-based compounds, like silane and silsesquioxane, have been proven to exhibit good hydrophobicity on cotton fabrics (Shirgholami et al., 2013). Daoud introduced a mixture of hexadecyltrimethoxysilane (HDTS), 3, 3 glycidyloxypropyl-trimethoxysilane (GTMS) and tetraethoxyorthosilicate (TEOS) to create a superhydrophobic surface on cotton with a water contact angle of 141°, but the durability of the fabrics was poor at low-temperature processes (Daoud et al., 2004). Roe and Zhang (2009) investigated the use of bis (triethoxysilyl) ethane and octyltrimethoxysilane in combination with silica nanoparticles to bring hydrophobicity onto the surface of the cotton fabrics with a water contact angle of 139°, even though the durability against rubbing was not satisfactory (Roe and Zhang, 2009). Satam et al. grafted fluorinated alkyl silane (FAS) onto cotton and nylon blended substrate to produce a superoleophobic surface (Satam et al., 2010). Tong studied the combination of fluorinated alkyl silane (FAS) and fluorinated-decyl polyhedral oligomeric silsesquioxane (FD-POSS), resulting in water repellent coatings on the surface of polyester fabrics (Zhou, 2013). The developed functional coating produced textiles with chemical resistance, self-cleaning and super water repellent with durability against different cycles washing (Huang et al., 2011, Wang et al., 2011). The combination of dodecafluoroheptyl methacrylate (DFMA) with waterborne polyurethane epoxy emulsion resulted in a sticky superhydrophobic but not oleophobic surface on paper (Huang et al., 2012). However, these hydrophobic surfaces have been challenged in terms of durability.

2.10.1 The theory of superhydrophobic surface

The term hydrophobic comes from the Greek words *hydro* and *phobic*, with the meaning water and fear (repelling water), respectively. It means to resist water droplets on a solid surface. In contrary, hydrophilic is also derived from the Greek words with *hydro* means water and *philia* means love (attraction to water). The water contact angle of a hydrophilic surface is usually less than 90° (Latthe et al., 2014). The hydrophobic surface is usually determined by the water contact angle of a water droplet persistent on a solid surface. The term ‘water contact angle’ is defined as a quantitative measurement of wettability or non-wettability, in which the liquid droplet maintains the position with the contact of a solid surface and the specific values of a liquid’s droplet volume or shape, the degree of the contact line or the angle of water droplet when it contacts with the solid surface or contact line are reported. The water contact angle of a hydrophobic surface is greater than 90° while that of a superhydrophobic surface is great than 150° (Kusumaatmaja and Yeomans, 2007).

There are two types of water contact angle to describe the superhydrophobic surface. When the water droplet is changing its volume or place on the title surface, it can be characterised in two observed angles such as advancing and receding angles. When the volume of the water droplet is increased, the maximum angle it can get is called the advancing angle. And when the volume of the water droplet is decreased, the smallest possible angle it can get is called the receding angle

(Li, 2017). The contact angle measurement during the growth and shrinkage is called advancing angle and receding angle, respectively. Difference between the receding angle and advancing angle is called the angle hysteresis (H).

Contact angle hysteresis (H) = advancing contact angle (θa) − receding contact angle (θr)

2.10.2 Surface tension

A superhydrophobic surface is dependent upon the surface energy and surface tension of the substrate. The surface energy and surface tension of liquids are numerically equivalent. The surface tension is a term used to describe the tension between the liquid molecules (Gorzkowska-Sobas, 2013). The cohesive force is present between molecules of the liquids (see Figure 2-1). The water molecules present in bulk form result in a cohesive force from the four sides of the neighbouring molecules. This means that the central water molecules have the net force of zero because all the four sides are subject to the same force of liquid that compensates each other. However, for some water molecules close to the corners cohesive forces from only three sides are applied and thus the molecules are pulled inwards, creating a possible small area of the surface that is under tension.

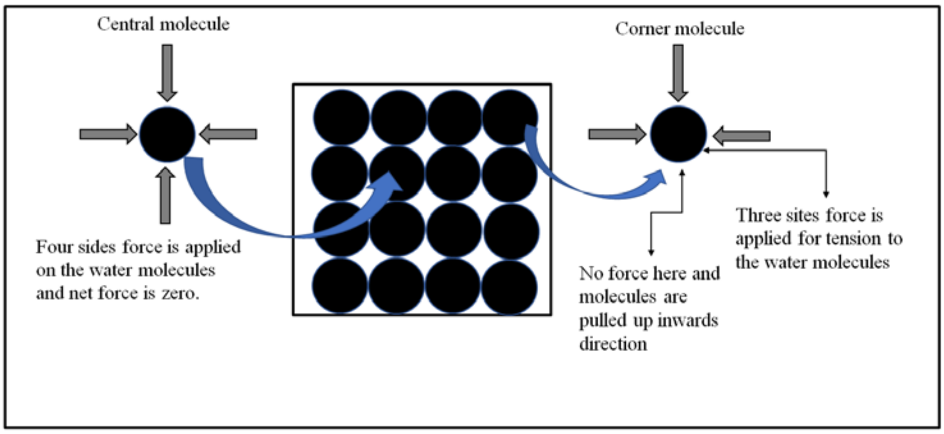

Figure 2-1: Interactions between the molecules in the bulk and close to the surface of a liquid. Forces acting on the molecules on the surface are not in equilibrium, and the molecules are pulled inwards (Gorzkowska-Sobas, 2013).

The surface tension is actually the cohesive force between the liquid molecules. Water molecules have a strong cohesive force between its molecules and the high surface tension values are 72 dynes/cm (Brzeziński et al., 2009). Cohesive force between the oil (n-heptane) molecules is weak and the surface tension value is 19.8 dynes/cm (American Association of Textile Chemists and Colorists, 2013c). Surface tension is used to explain the density and heaviness of liquid molecules. Surface tension depends upon the cohesive force (weak or strong) between the liquid molecules. The surface tension (strong cohesive force) of water is higher so that it sits down in a mixture of water and oil, while the lower surface tension (weak cohesive force) of oil results it on the top of the mixture (see Figure 2-2).

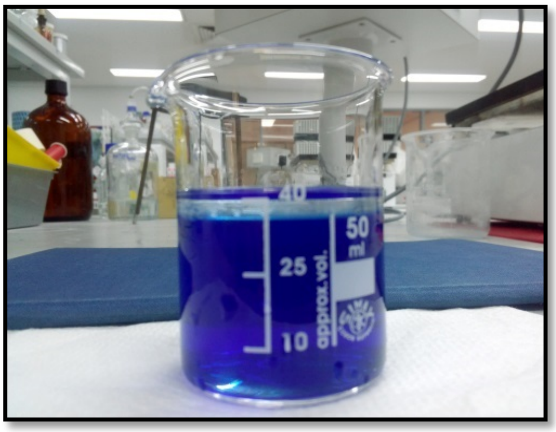

Figure 2-2: The mixture of water and oil. Oil has low surface tension and sits on top of the surface of water solution due to its high surface tension, surface energy and gravity.

The boundary force applies to only three sides and makes changes in the volume, shape and energy of the liquid molecules. The concept of surface tension means that when a liquid droplet has a greater density as compared to water droplets (1,000 kg/m³), it is able to sit or doesn't move on the surface (Gorzkowska-Sobas, 2013). For example, a mixture of water and oil droplets usually shows the oil sits on the water solution surface, because the surface tension or gravity of oil is less as compared to a water molecule (see Figure 2-2). All the surface tension of chemicals was shown in Table 2-2.

Table 2-2: Surface tension value of water, oil and liquids chemicals and warfare agents (Pan et al., 2012).

Chemical name	**Surface tension (dynes/cm)**
n-Hexane	18.4
n–Heptane	19.8
Triethylamine	20.7
Methanol	22.1
Isopropyl alcohol	23.0
Acetone	23.2
n-Decane	23.8
Paraffin oil	26.0
Tetrahydrofuran	26.4
Dichloromethane	26.8
n-Hexadecane	27.3
Acetic acids	27.0
Toluene	28.4
Acetonitrile	28.7
Dimethylformamide	36.7
Butadiene	47.0
Water	72.8
Sodium hydroxide	101.0
Chemical warfare agents	
GB	25.9
GD	24.5
VX	31.3
GF	32.3
Sulphur mustard gas (HD)	42.5

2.10.2.1 Young’s theory

Young explained the situation when a water droplet was in a rest condition. The water droplet is in the balance position when the effective force from three sides by the atmosphere or vapour molecule as shown in Figure 2-3. The water droplet spreads out until the equilibrium is achieved. The contact angle of the water droplet is called the contact angle (θ) on a flat surface but not applicable on a rough surface (Li et al., 2007, Xue et al., 2010).

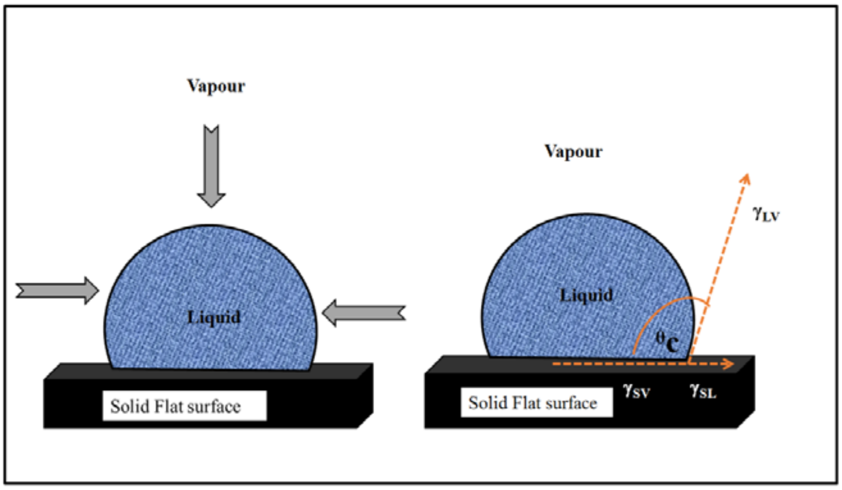

Figure 2-3: Different surface tension of solid, liquids, and vapour phase according to the Young’s theory (Xue et al., 2010).

The water droplet applies surface tension on solid to vapour condition ($^{\gamma}$sv), solid to liquid ($^{\gamma}$sL) and liquid to vapour ($^{\gamma}$Lv), respectively. Young explained the behaviour of the water droplet only on a flat surface by equation (1):

$$\boldsymbol{cos\emptyset} = \left(\frac{(^{\gamma}\mathbf{sv} - {}^{\gamma}\mathbf{sL})}{^{\gamma}\mathbf{Lv}}\right) \qquad (\mathbf{1})$$

The contact angle (θ) of a water droplet can measure the wettability of a flat surface. The surface roughness was explained in the earliest work of Wenzel and Cassie Baxter theory.

2.10.2.2 Wenzel’s theory

The basic theory of superhydrophobicity was explained by Wenzel in 1934. According to this theory, the main emphasis on wettability or hydrophilic phenomena depends upon the size of the contact angle (see Figure 2-4). The water droplet on a rough surface shows different behaviour of contact angle. The rough surface has some grooves for the water droplet to fill in or penetrate through and thus smaller contact angle is shown on the surface (Koishi et al., 2009, Roach et al., 2008).

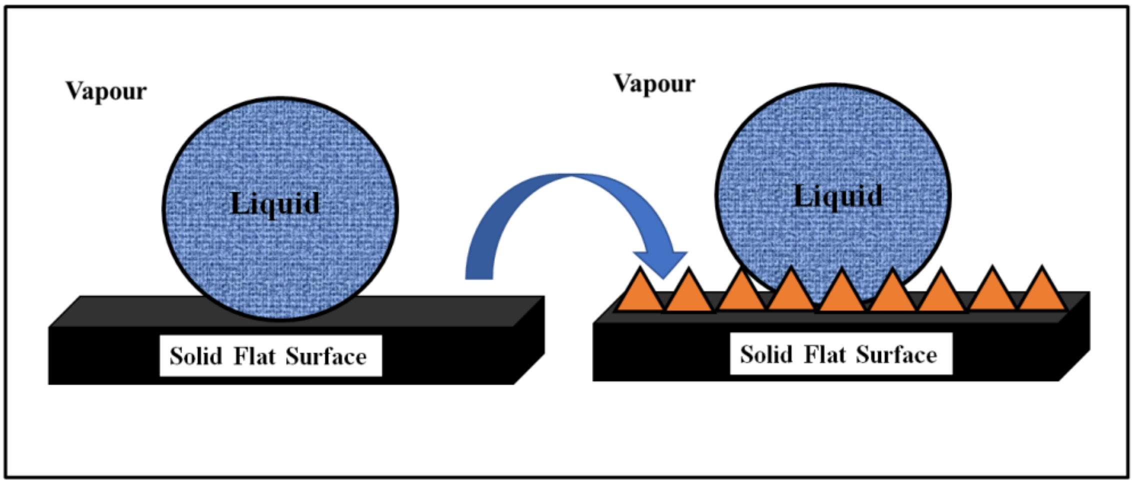

Figure 2-4: The solid, liquids, and vapour phase according to Wenzel's theory (Chinchwade et al., 2014).

Wenzel's theory explains the hydrophobic quality by following equation (2):

$$\cos \emptyset eW = r \cos \emptyset \qquad (2)$$

Where,

W refers to Wenzel theory

r refers to surface roughness

Øe stands for the equilibrium contact angle on the smooth flat surface.

Øe stands for the contact angle as the effect of surface chemistry.

The surface roughness factor r is equal to 1 for a smooth surface. When the r is greater than 1 for a rough surface, the surface ratio on the flat and rough surface is equal and the equilibrium condition will be maintained. The contact angle of the water droplet sits on the surface. If the value of the contact angle is less than 90°, the surface roughness is much less likely to show the wettability or hydrophilic property of the surface. When the value of the contact angle is greater than 90°, it means the surface roughness clearly shows the non-wettability or hydrophobic property of the surface. The surface roughness has some rough grooves to trap the water droplets or air bubbles, which contributes to the non-wettability of the surface. While this theory considers the surface roughness r and the effect of surface chemistry Øe, the wetting behaviour of the water droplet in a different situation has been described by Cassie Baxter (Li, 2017).

2.10.2.3 Cassie Baxter’s theory

In 1944, Cassie and Baxter explained the interface of a liquid surface, which consists of two phases, namely the solid-liquid and liquid-vapour interfaces. The contact angle of two states is explained in the equation (3). Two interfaces of a liquid surface show the bridge formation of an air gap or pocket between the water droplet and the solid surface. The water droplet does not touch the surface and thus there is no surface roughness. The scenario of the contact angle between an air gap and the flat surface is shown in Figure 2-5, and the sum of all contact angle (Θ1, Θ2) and surface fraction (f_1, f_2) between the two liquid-vapour phases are described as below.

$$\cos \Theta c = f1 \cos \Theta 1 + f2 \cos\Theta 2 \qquad (3)$$

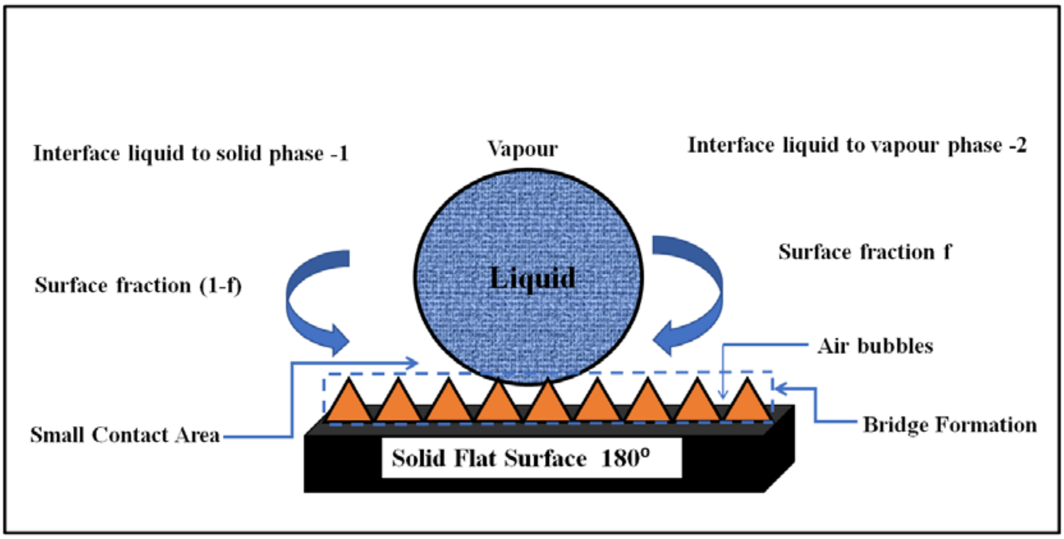

Figure 2-5: The solid, liquids, and vapour phase according to Cassie Baxter’s Theory (Li, 2017).

The cos Θc shows the contact angle of Cassie and Baxter’s equation. This equation applies to the liquids-vapour surface fraction with (f) and also the same solid fraction donated with (1-f) on the wetted surface by the liquid droplet (Li et al., 2007). The surface fraction of vapour (f) and the contact angle was cosΘ. The surface fraction of liquid-solid is (1-f) and the contact angle is cos180° on the flat surface. The surface fraction from vapour to solid surface can be calculated by equation 2 and the resulting angle represents on the wetted surface. The surface fraction of liquid to solid surfaces, as denoted by (1-f) on the flat surface with the contact angle of 180^0 as described in the equation below, is used to calculate the resulting contact angle of the wetted surface.

$$cos\Theta c \;=\; f\, cos\Theta \;+\; (1 - f\,)\, cos180^0$$

$$where\;, the\; contact\; angle\; on\; the\; flat\; is\; cos180^0 \;=\; 1$$

$$cos\Theta c \;=\; f\, cos\Theta \;+\; (1 - f\,)$$

$$cos\Theta c \;=\; f\, cos\Theta \;+\; f - 1$$

The value of surface fraction (f) ranges from 0-1. When the value of f is 0 it means the water droplet does not touch the surface at any time. If the value of f is 1, it means the water droplet just fills all grooves on the surface with a completely wetted surface just like the case of a flat surface. So, the first situation with the surface fraction of zero is to explain the small area of water droplets contacting the solid surface and water droplets easily rolling over the surface, according to the Cassie and Baxter's theory. The contact angle is increased for the bridge formation with the increased air gaps between the two stages, so that water droplets easily roll over the surface.

2.10.2.4 Transition between Cassie and Wenzel States

The combined equation of Wenzel and Cassie and Baxter shows the uneven surface and defines the high hysteresis or sliding contact angle of water droplet rolling off in both directions. However, the measurement of the contact angle was not determined due to the water droplet sticking to the uneven surface and filling the air gaps (Kusumaatmaja and Yeomans, 2007). According to Wenzel, the water droplet is resting on an uneven surface, showing a contact angle greater than 90°. It means the water droplet sticks to the surface without penetrating inside the substrate. Cassie and Baxter's theory can be used to explain the slippery behaviour of water droplets, namely their rolling off on the surface.

The slippery behaviour demonstrated the rolling off the property of water droplets on the surface. When the water droplets stay in between the air bubbles and surface grooves then the water droplets adhere on the surface, regardless of the contact angle for an uneven surface. This theory is not a successful way to measure the surface roughness, fraction and contact angle of multi-layers. Cassis and Baxter explained the bridging phenomenon of holding water droplets on the top surface. However, Wenzel's theory explained the transition state of external energy being converted into electrical or vibrational energy or the transferring of water droplets from one phase to another phase (Roach et al., 2008). A superhydrophobic surface has a lot of interesting features, both in academia and from an industrial point of view due to its resistant properties. Recently, progress has been made in the preparation, theory, modelling and application techniques of superhydrophobic surfaces with fluoro-polymers. The main direction of the superhydrophobicity theory was to explain the science in different ways. Wenzel and Baxter and Cassie's theory explained the different conditions of global or free energy calculation and moulding dimension structure. Boltzmann explained the theory of 3D system and modelled the height of energy barrier transferring between the one places to another place or spreading out over the large surface area. Researchers described the metastable and chemical pattern of superhydrophobicity with the help of calculation methods (Kusumaatmaja and Yeomans, 2007, Li and Amirfazli, 2007, Marmur, 2004). Scientists are focusing further on extended theories, effects, features, factors and surface functionalization process with different types of materials (Reyssat and Quéré, 2009, Gao and McCarthy, 2007, Latthe et al., 2014, Whyman et al., 2008, Kwon et al., 2009).

For textile fabrics, there are four types of hydrophobic surface that provide different repellency properties such as an ultra-hydrophobic, superhydrophobic, oleophobic and the omniphobic surface (Chinchwade et al., 2014). A hydrophobic surface means the contact angle is greater than 90° to control the resistance to water with no penetration occurring inside the fabric. An ultra-hydrophobic surface means the contact angle is between the ranges of 120°-150°. A superhydrophobic surface has three kinds of a special surface for which it provides resistance to oil, water and chemical. A superhydrophobic surface means the contact angle is in between the range of 150°-170°. An oleophobic surface means the excellent resistance to all kinds of oil or oily nature of chemicals, such as n-Hexadecane, n-Heptane and n-Decane. An omniphobic surface means the excellent resistance to all chemicals, namely acetic acids, sodium hydroxide, dimethylformamide, n-hexane, butadiene and isopropyl alcohol etc (Pan et al., 2012).

2.11 Application of the superhydrophobic coating

The superhydrophobic surface was successfully produced using artificial methods of surface modification. Surface modification is a very helpful method to enhance surface roughness with a high contact angle. Superhydrophobic surfaces were prepared by approaches with two different categories for different practical applications. One category is the top-down approaches such as lithographic, plasma technology, templation, sublimation and sol-gel methods. The other category is the bottom-up approaches include chemical deposition, layer-by-layer (LBL), covalent bonding, colloidal assembles, electrospinning and electrospraying.

2.12 Top-down approaches

2.12.1 Lithography

Lithography involves a number of imprints of repeated patterns of the moulding process, and it has a light irradiation layer with desired features of coating but is also photo-resistant. This approach is based on long life usage of silicone materials, and the heat and pressure are used to make the small design on the layering of thermoplastic polyurethane polymers. Nano-imprint lithography is used in this process to make the master design. The lithography approach involves a superhydrophobic surface that is produced by the etching step of salinization (Li, X-M, and Reinhoudt & Crego-Calama 2007).

2.12.2 Plasma technology

The plasma technology is used for the preparation of superhydrophobicity, water repellency, conductivity and dye-ability of the fabric surface. Plasma technology is eco-friendly, using low input energy and dry etching techniques. Surface roughness can be easily obtained with a high water contact angle of fabrics. Plasma techniques depend upon the different types of gas including tetrafluoro-methane, ammonia, and argon or oxygen, and different vacuum mode for low and high pressure (Dubas et al., 2006). Plasma treatment requires specific equipment and is not suitable for bulky treatment.

2.12.3 Templation

The template approach is defined as replicating of moulding and dissolution of the template. The template approach provides the lotus effect with natural materials. Templates are used to create the polymeric coating with a superhydrophobic surface. The template is used for a positive and negative replicating of micro or nanostructure, resulting in the natural lotus effect with the water contact angle of 160^0. The template produces the nanotexture of mountains and repetition of hierarchical structure. But this negative repetition shows the contact angle of 110° while for the positive repetition it shows the contact angle of 160°. The difference in the contact angle is due to the different roughness of the surface of fibres, and it may result in different oil repellency on the fabric surface (Kim, 2008).

2.12.4 Sublimation

Sublimation is the chemical process of solid materials directly converting into gas formed without the liquid state. Sublimation is helpful in producing lightweight structure of surface roughness to enhance the fabrication of superhydrophobic surface on silica films. The sublimation of aluminium acetylacetone was applied during the calcination process to create a transparent film with the superhydrophobic surface. Fluoro-alkyl polymeric coating by sublimation also enhances the surface roughness of fabrics (Zhang et al., 2008).

2.13 Bottom-up approaches

2.13.1 Sol-gel method

The Sol-gel method is an approach to conversion of monomers into colloidal solution (sol) that transfers into nanoparticles (gel). This sol-gel preparation is time-consuming and expensive. The method of sol-gel combining with electrospinning was widely used in the continuous preparation of nanofibres and textiles. The sol-gel approach involves the hydrolysis of nano-oxides in the presence of a large amount of solvent. It is helpful in the preparation of gel formation of ortho-silicate. It is used on its own or to be combined with a special filler of silica nanoparticles. The sol-gel approach was also used to enhance the surface of fabrics by integrating a functional group with a high contact angle. Sol-gel method is not feasible to be the lining of a protective suit (Brzeziński et al., 2009, Hikita et al., 2005, Ramaseshan and 2007, Latthe, 2009).

2.13.2 Chemical deposition

A Chemical deposition approach involves the chemical reaction with inorganic metals on the substrates, resulting in the deposition of very thin films on the substrates. The inorganic metals such as Zns, CdS, CuSe and InS are commonly used as the depositing materials. Chemical deposition is described using different terminologies, such as chemical bath deposition (CBD), chemical vapour deposition (CVD) and electrochemical methods (Zimmermann et al., 2008). This technique is used to create nano-pins, nano-tubes and nano-rods.

2.13.3 Colloidal assemble

Mono-dispersion of polystyrene beads creates a bead-like structure on the substrate by the spin coating method. This structure can also be controlled by oxygen plasma techniques that are suitable for laboratory condition. The polystyrene and silica nanoparticles were involved to create the hierarchical structure of surface roughness (Wang et al., 2006). The colloidal crystal film of polystyrene–n-butyl acrylic acids can be well tuned to control the wettability of fabrics by the chemical composition methods. These techniques are very cost-effective for the textile sector.

2.13.4 Layer-by-layer deposition

Layer-by-layer techniques were introduced by Decher (Decher and Schmitt, 1992), which involved the layering on a substrate. Layer-by-layer techniques make it easy to control the thickness of the coatings and to increase the electrostatic charges such as polyanion and polycation between two layers. Layer-by-layer deposition is useful for cotton fabrics with additional properties including self-cleaning, hydrophobicity, water repellency and antibacterial activity. The surface roughness of a substrate is usually created by the nanoparticle layers, and the interaction between the first layer and the substrate was usually activated by positive and negative ions.

2.13.5 Covalent layer-by-layer assembly

Layer-by-layer is an assembly approach that uses covalent bonds to form the multilayer grafting, which is more durable, stable and practical; it is a versatile way to construct thin-film with nano-composition on the surface of substrates. This technology is popular because it is simple and it allows hydrogen to the bond between the substrate and materials. It is most commonly used to fabricate an interface involving a multi-layer ionic assembly of polyelectrolytes. However, some ionic assemblies are of limited applicability because of the weak interaction between the substrate and the layers. The chemical reaction between two layers is very important and it affects the durability and stability of the coating as well as the feasibility of the process. Usually, the functionalized nanoparticles are used in the process. After layer-by-layer assembly, the outer surface usually contains residual functional groups, which can react with low surface energy agents by using covalent bonding (Yüksekkaya, 2008, Xue et al., 2010).

2.13.6 Electrospinning

Electrospinning is a common method for the preparation of nanofibres. The process consists of an extruder nozzle, a ground collection plate and the electrical bias to produce electrospun films with the lotus effect. This process has been applied to the fabrication of superhydrophobic films from polymers along with the evaporation of the solvent. This technique requires polymer materials with a lower molecular weight and with the hydrophobic and oleophobic surface. Electrospinning method can be used to optimise the rough surface together with other methods of chemical vapour deposition and sol-gel methods (Li et al., 2007).

2.14 Textile materials

Cotton fibres are the most favoured and widely used fibres in the textile industry. Cotton fibres are derived from plants. The cotton plants give us fruit is called bolls. After the mature crop of cotton are picked and ginned and separate into the fibre known as cotton lint. Cotton lint is used in the same way as seed, stalks and seed hulls. Unfinished cotton is used as greige fabrics. India was cultivated in ancient times for cotton fibres. Cotton fibre contains the composed structure of the long chain of cellulose molecule. It involves binding force to combine the whole structure firm and straight. Unite of the cellulose are repeated in the cotton fibres as shown in Figure 2-6.

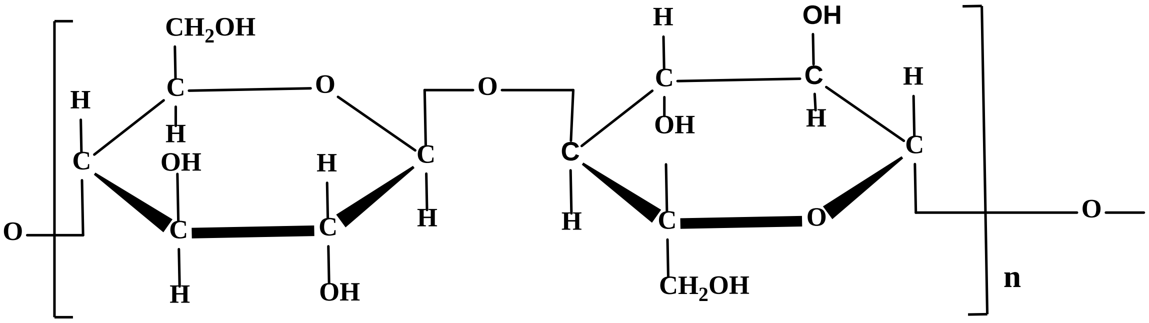

Figure 2-6: Chemical structure of cotton (Perincek et al., 2007).

Cotton fibres are also used an ideal production in denim jeans, bed sheets, t-shirt, shirt, nappies, socks, towel, tarpaulins, tent and pharmaceutical and medical supplies and astronaut’s flight space suits. Cotton fibres are the most popular and famous fibres in the textile industry used as a wide application. A number of studies have described the water repellency and superhydrophobic surface so as to improve the wettability of cotton fabrics (Deng et al., 2010, Li et al., 2007, Roe and Zhang, 2009, Ramaseshan and 2007).

2.15 Summary

The previous study has contributed to the surface science in terms of chemical protection. With the advanced materials being employed and novel fabrication techniques being developed, today’s chemical protective textiles aim to be more versatile protective and durable without compromising comfort. This research bases on the safe polymeric coating of WPU, TPU and Rubber membrane with the combination of repellents and the superhydrophobicity on the surface of fabrics. The alternative compounds of fluoro-polymers such as oleophobic, phobol and trimethoxysilane and polydimethylsiloxane were used as repellents.

The superhydrophobic surface was developed by the layer-by-layer methods via knife-pad-knife-cure coating. The superhydrophobic surface was produced on the two coated layers with the help of cross-linking agents on cotton fabrics, resulting in a low surface tension on the cotton fabric as well as enhanced resistance to water, oil and chemicals with altered comfort properties.

3 MATERIALS, METHODOLOGY AND MEASUREMENTS

Chapter 2 described the background and literature review on chemical protection. This chapter explicates the design of experimental work to follow the aim and objectives of this research (see Chapter 1). In this chapter, information about the materials, methods of coating and testing evaluations are detailed.

3.1 Materials

To study of cotton fabric with different of silane compounds, nanoparticles and different coating methods to produces the superhydrophobic surface. The contact angle, laundering and rubbing fastness properties of fabric were measured with different techniques. The water repellency of cotton fabric was improved to the behaviour of resistance for water, oil, and stain. The challenge of the durability of cotton fabric still is present at this time. The treatments with polyurethanes coating with repellents found the better result as for laundering, oil and chemical resistances for fabrics as compare to the fluoro-polymers. The achievable result depends upon the types of coating and factors are very important to retain the water, oil and chemical resistance of the superhydrophobic surface of the fabric. All the specification of chemicals and materials as described in Table 3-1.

Table 3-1: Specification of materials, chemicals and suppliers.

Materials	**Supplier**
Binder	
ICB Tubicoat Fix iso-cyanates	CHT Pty Ltd, Australia
Invadine PBN, Kinttex ®	Huntsman Singapore Pty Ltd
Isys HPx	CHT Pty Ltd, Germany
Membrane	
Silastic 1941-200P (LSR (part-A+B), Rubber membrane	Dow Corning Europe S. A, Beligum
Thermoplastic polyurethane (TPU, Texalan -598-A)	Pacific Urethanes Pty Ltd, Australia
Tubicaot I665 (WPU Membrane)	CHT Pty Ltd, Australia
Repellent	
Fel, Phobotex Rsh,	Huntsman Singapore Pty Ltd
Olephobol® CP-C	Huntsman Singapore Pty Ltd
Phobol® CP-C	Huntsman Singapore Pty Ltd
Trimethylmethoxysilane (TMMS)	Sigma Aldrich Pty Ltd, Australia
Xiameter (FBL-O563) PDMS-TMS	Dow Corning Pty Ltd, Australia.
Chemicals	
Acetic acid	Ajax Fine. Chem PTY. Ltd Australia
Acetone	Ajax Fine Chem Pty Ltd Australia
Acetonitrile	BDH Limited Poole, England.
Butadiene	BDH Limited Poole, England.
Dichloromethane	BDH Limited Poole, England.
Dimethylformamide	Merck, Germany
Isopropyl alcohol	BDH Limited Poole, England.
Methanol	Honeywell International Inc. USA
Mineral oil	Johnson and Johnson Pacific Pty Ltd, Australia
N-decane	Sigma Aldrich Pty Ltd, Australia
N-Heptane	RCL LAB SCAN Limited, Australia
N-hexadecane	Sigma Aldrich Pty Ltd, Australia
N-hexane	Ajax Fine. Chem PTY. Ltd Australia
Sodium Hydroxide	Chem Supply Pty Ltd, Australia.
Sulphuric acid (98%)	RCL LAB SCAN Limited, Australia
Tetrahydrofuran	BDH Limited Poole, England.
Toluene	Rhone May & Baker Pronalys Chemicals Pty Ltd, Australia

3.1.1 Materials specification

All the fabrics used in this work are summarised in Table 3-2.

Table 3-2: Specification of fabrics.

Materials	**Cotton**	**Polycotton**	**Cotton**
Fibres	100% Cotton	80/20 Cotton /Polyester	100% Cotton
Construction	Plain	3/1Twill	Plain
Fabric thickness (mm)	0.56	0.58	0.34
Thread density (Warp/cm)	33	33	25
Thread density (Weft/cm)	15	20	25
Fabric weight (g/m^2)	150	180	160

3.2 Methodology

The method that used to coat fabrics is summarised here while specific recipes will be detailed in Chapter 4-7 accordingly.

3.2.1 Scouring

The cotton fabric was wetted by 0.01% (w/v) Triton X-100 solution in water for 30 minutes and scoured by caustic soda at 90°C for 1 hour. The fabric was rinsed with warm water and then with cold water, followed by an overnight hanging dry.

3.2.2 Pad batch methods

The Ernst Benz Pad machine was used to coat the cotton fabric. Two parallel rollers, one moving and the other stationary, were used to pad the fabric from both sides. The fabric passed down through these rollers into the liquid and then comes back up through the rollers (see Figure 3-1). The pad-batch method applies pressure to the fabric which reduces the thickness of the fabric. The pressure applied to the fabrics was around 8 kPa/cm.

Figure 3-1: Pad batch process of fabric.

The fabric was weighted before and after the padding to calculate the wet pick up percentage. The formula is shown below:

$$\text{Pick up\%} = \frac{\text{Rolled weight of the fabric} - \text{Dry weight of the fabric}}{\text{Dry weight of the fabric}}$$

3.2.3 Knife edge coating

The scoured cotton fabric was subject to a three-step using the coating as Pad (Binder)–Knife (Membrane/polymers)–Pad (Repellent) methods. Knife coating machine is a simple technique which is applicable for a single layer coating of the textile substrate. A vertical sharp knife blade scrapes over the stretched fabric in a frame. The coating paste is applied to one side and the blade spreads the paste over the fabric, see Figure 3-2. The blade was 0.01 mm from the fabric.

3.2.4 Drying and curing

Drying is a simple method to dry the fabrics at room temperature in the air or laboratory oven at 60°C for 30 minutes. In drying methods, the liquid portion of the solution is evaporated from the surface of fabrics. In the drying process, the liquids are converted into vapour and evaporated from the surface of fabrics. Sometimes this creates a problem with humidity and temperature of a laboratory. So, the best way is dry in a laboratory oven. The curing unit was used to maintain a standard condition for the environment, with the temperature at 150°C and 3 minutes to dry the fabric. This curing unit is very helpful for the fixation of the coating, as well as straightening the fabric (Figure 3-3)

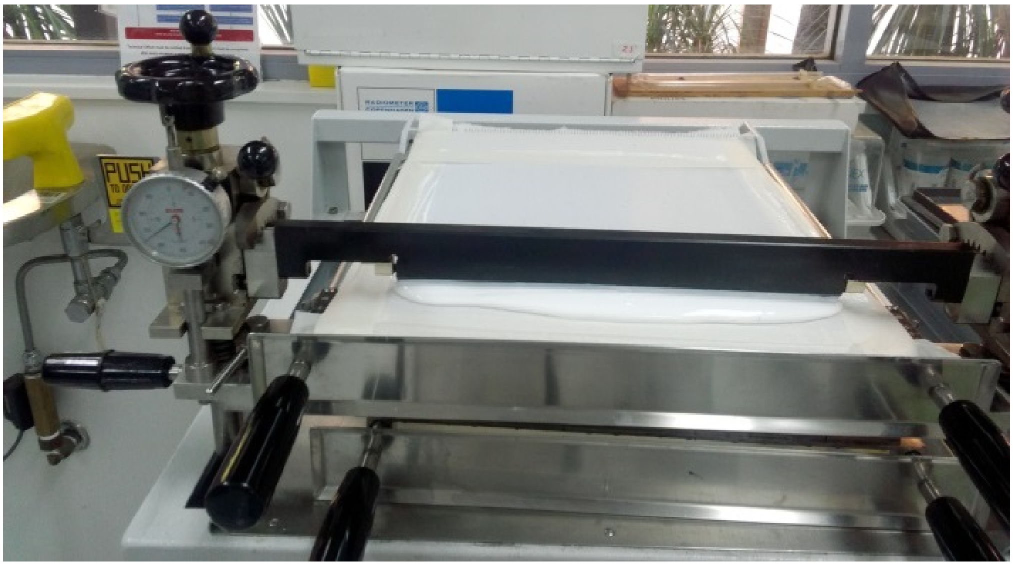

Figure 3-2: Knife edge roll over coater.

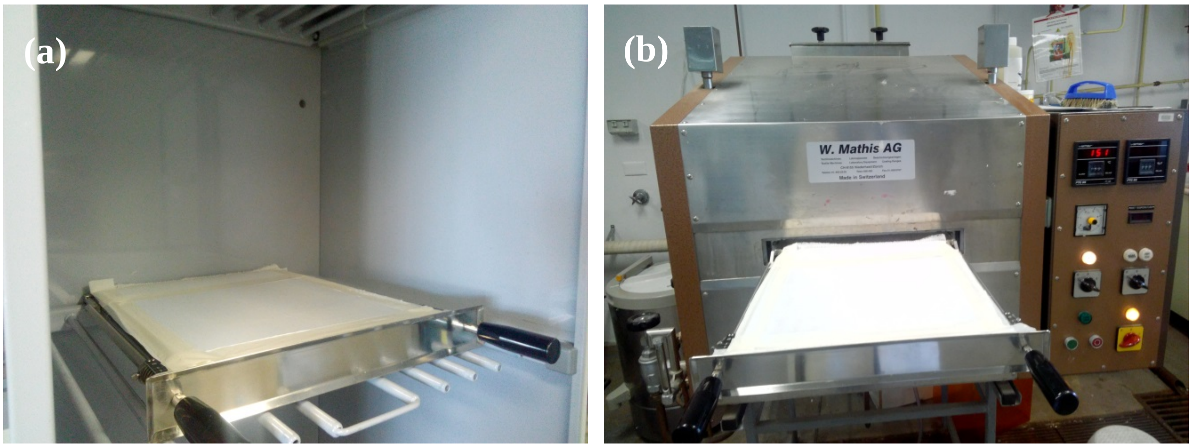

Figure 3-3: Laboratory oven (a) and curing unit (b) to dry the coated fabric.

3.3 Measurements and characterization

3.3.1 Thickness and GSM measurement

The thickness of the coating was calculated using a thickness tester (British Indicators Ltd, St. Albans) according to the AS 2001.2.14 method (Australia Standard 1989). The actual thickness of fabric surface was measured both before and after coating. The thickness dial gauge was zeroed. The anvil and the foot were in contact with the fabric tested for 10 seconds and the thickness was measured on the dial gauge. Each coated fabric was tested ten times at different locations on the fabric and the average was calculated from the ten readings to find the thickness of the fabric coated surface.

The gram per square meter (GSM) cutter (Zweigle) test was used to calculate the weight of the fabric according to the Australian Standard AS-2001.2.13 (Australia Standard 1987). The average weight was calculated using ten test samples of both the uncoated and the coated fabric. Summary of all test method was available in Table 3-3.

Table 3-3: Summary of test methods, equipment and manufacture details.

	Test	**Method**	**Equipment**
1	Contact Angle measurements	Sessile Drop Method	Contact angle system Data Physics, OCA 20, Germany
2	FTIR spectroscopy	-	FTIR spectrophotometer Perkin Elmer 300, USA
3	SEM image	-	FESEM, Quanta™-200, UK
4	Fabric conditioning	AS 2001.1-1994	Conditioning cabinet
5	Thickness	AS 2001.2.14-1989	Thickness tester British Indicators Ltd, St. Albans
6	GSM	AS-2001.2.13-1989	GSM cutter, Zweigle, Germany
7	Crock fastness	AATCC 08-2013	Crock meter, Toyoseiki, Tokyo, Japan
8	Laundering fastness	AATCC 61-2013	Launder-o-meter, SDL Atlas, UK
9	Air permeability test	AS 2001.2. 33-1990	Air permeability tester, M021S, SDL Atlas, UK
10	Pilling resistance test	ISO-12945- 2-2000	Martindale Pilling Tester, SDL Atlas, UK
11	Fabric stiffness test	ASTM D1388-14-2012	Shirley stiffness tester, John Casartelli Limited, England
12	UV irradiation test	ASTM G155-2012	Weather-o-meter, Ci 4000, SDL Atlas, UK
13	Thermal and water vapour resistance	ISO 11092:1993(E)	Sweating Guarded Hotplate (SGHP), SDL Atlas, UK
14	Moisture management test (MMT)	AATCC TM 195-2009	Moisture Management Tester, SDL Atlas, UK
15	Grab test	ASTM 1682-1988	Tensile strength tester, INSTRON, USA
16	Hydrostatic pressure test	AS 2001.2.17-1987	Hydrostatic pressure tester, IDM Instrument Pty Ltd, Australia
17	Water repellency spray test	AATCC 22-2010	Spray rating tester, Toyoseiki, Tokyo, Japan
18	Aqueous liquid repellency test	AATCC 193-2012	no Equipment required
19	Oil repellency test	AATCC 118-2013	no Equipment required
20	Chemical resistance test	-	no Equipment required
21	Soil repellency test	AATCC 130-2014	no Equipment required

3.3.2 Water contact angle measurements

The water contact angle was measured using a contact angle system (Data physics, CA20, Germany) at room temperature. A droplet size of 4 microlitre of ultra-pure water from a Milli-Q filtration system was used to evaluate the contact angle. A fixed needle was mounted 10 mm above the tilting table on which the fabric sample was placed. The syringe was placed so that a droplet from the needle contacted the substrate. This allowed for the transfer of the droplet from the needle tip onto the surface of the fabric. A photo was taken to calculate the contact angle by Sessile Drop Method. The contact angle values were averaged from six readings taken at different places on the fabric.

3.3.3 FTIR spectroscopy

ATR FTIR spectroscopy was used to determine the chemical changes of uncoated and coated surface of the fabric. An attenuated total reflection infrared spectroscopy (ATR-FTIR) spectrum was reported for each of the samples using a spectrophotometer (Perkin Elmer 300, USA) with a diamond crystal. A single layer of fabric was placed on the ATR crystal and then the pressure clamp was lowered to provide good contact between the sample and crystal. The scanning ranges of spectra were 4000-650 cm^{-1}.

3.3.4 Scanning electron microscope

Field emission scanning electron microscope (FESEM, Quanta™-200, UK) was used to study the surface morphology of the coated and uncoated fabrics. The instrument was set at a pressure of 0.34 Torrs and voltage of 10keV and the analysis was conducted at room temperature. The samples were prepared with sputter coating (IMBROSE, Spi A20014, Australia) using a thin layer of gold particles.

3.3.5 Crocking fastness test

A crock meter (Toyoseiki, Tokyo, Japan) was used to determinate the durability to rubbing of the coated surface of the fabric. Specimen sizes of 130 mm x 40 mm were prepared in both the warp and weft directions for wet and dry testing. The samples were tested for 10 complete turns at the rate of one turns per second to slide the finger back and forth 20 times, in accordance to AATCC 08: 2013. A crock meter test cloth was used to determine the crocking fastness with a downward finger force of 9 N (American Association of Textile Chemists and Colorists, 2013a).

3.3.6 Laundering fastness test

Accelerated laundering tests were performed in accordance with AATCC 61: 2013 (1A) cycle. The fabrics were washed in an SDL Atlas Launder-o-meter at 30°C along with 10 steel balls and AATCC Reference Detergent that did not contain any optical brightener. One washing cycle 45 minutes is approximately five typical commercial launderings. Each specimen was twice hand rinsed with deionized water then dried in an air circulating oven for 30 minutes. All samples were conditioned based on ISO 139 at a temperature of 20 ± 2°C and a relative humidity of 65 ± 4% prior to testing (American Association of Textile Chemists and Colorists, 2013b).

3.3.7 Air permeability test

To provide an indication of the breathability of the coated fabrics, the fabrics were tested for air permeability. Air permeability is defined as the volume of air in millilitres that passes through 100 mm^2 of a fabric at a pressure difference of 10 mm head of water in one second. Airflow of coated and uncoated fabrics was measured ten times with the air permeability tester (SDL Atlas Pty Ltd, England) using AS-2001.2.33: 1990 standard (Australia Standards, 1990). During the test, the specimen is clamped over an air inlet of the apparatus and air is sucked through it by means of a pump. The air valve is then adjusted to give a pressure drop across the fabric of 10 mm head of water and the airflow is then measured using a flow meter. Ten specimens were tested and the mean air flow in cubic centimetre per square centimetre per second was calculated from the ten specimens reading for average results. The calculation of the air permeability of the fabric by used this formula:

$$\text{Air permeability (L)} = \frac{\text{Rate of air flow of specimen (V)}}{\text{Area of fabric (A)}}$$

Where

L = air permeability, in cubic centimetres per square centimetre second

V = rate of air flow, in cubic centimetres per second

A = area of fabric under test, in square centimetres

3.3.8 Pilling resistance test

Pilling refers to the formation of surface dust balls that mix up with fibres and shift into pills. These pills are created during wearing and washing process in which the fabrics are affected with frictional force. The friction force is the cause of pilling of fabrics. Fabrics defects are usually judged by Martindale Pilling Tester (SDL Atlas international, England). The assessment of fabrics followed the pilling methods ISO 12945-2: 2000 (International Standards Organization, 2000). The specimens were prepared in the circular shape with help of a cutter, from both warp and weft directions. The specimen and foam were fixed in the given upper plate and mounted properly into the downward direction. The upper plate was then put in the instrument holder and was fixed into the centre of the lower plate. The yoke holder was then put on the top side of the lower plate. The pressure plate at 9 kPa was loaded to stop the vibration of the upper plate at the start of the test. The specimen was subject to free direction rubbing for 50, 500, 1,000 and 2,000 cycles. After the completion of abrasion cycles, the durability of the coating was measured accordingly. The standard photographs and rating were done to assess the pilling resistances of fabric as authorized by ISO (Table 3-4).

Table 3-4: ISO Standard test for pilling resistances.

Rating	**Surface evaluation**
5	No pilling
4	Slightly pilling
3	Moderate pilling
2	Severe pilling
1	Very severe pilling

3.3.9 Fabric stiffness test

The fabric stiffness is defining as the function of elastic or flexibility modulus against its own weight. The area of bending fabric is known as bending stiffness or flexural rigidity. Shirley stiffness tester (John Casartelli Limited, England) was used to conduct the stiffness rest according to the standard ASTM D1388-14 (American Society for Testing and Materials, 2012b). Cantilever test is widely used to determine the fabric stiffness in the practical application. All samples were conditioned based on ISO 139 at a temperature of 20 ± 2 ^{o}C and a relative humidity of 65 ± 4% prior to testing. Four specimens with the size of 25 mm x 75 mm were prepared in both the warp and weft directions. The specimen was placed along the horizontal direction on the flat surface of the stiffness tester with its edge matched with right-hand side of the tester marked as zero. The slide was then slightly moved for the specimen to touch the knife edge at an angle of 41.5^{o}. The overhanging length of fabric was recorded as the bending length, and flexural rigidity was calculated from the bending length and the fabric weight accordingly.

Fabric stiffness is measured the bending length and calculated with Flexural rigidity by using the formula:

$$G = 1.421 \times 10\text{-}^{5\,\times}\, W c^{3}$$

Where:

G = flexural rigidity, μjoule/ m,

W = fabric mass per unit area, g/m^2, and

c = bending length, mm.

And the units of the constant (1.421×10^{-5}) are mg/cm.

Flexural rigidity is calculated for warp and weft ways of fabrics and over all flexural rigidity is calculated as geometric mean those two values. Overall flexural rigidity (Go).

$$Go = (Gw.\ Gf)^{\frac{1}{2}}$$

3.3.10 UV irradiation resistance test

The ultraviolet (UV) irradiation resistance test was used to analyze the effect of UV light exposure on the coating. UV irradiation reduces the end life of garments and causes colour changes of the coating. UV resistance was performed on a Weather-o-Meter (Ci 4000, SDL Atlas Pty Ltd, England) according to the standard ASTM G155 (American Society for Testing and Materials, 2012a). A Xenon arc lamp was used to expose the fabric to high-intensity UV rays. The uniform exposure of UV radiation source was used to ensure the UV flux in the environment chamber at 340 nm wavelength. The specimen was cut into a rectangular shape with the size of 20 cm x 5 cm for each fabric in both warp and weft directions. Specimens were exposed to UV light at 40^{o}C and relative humidity 50% (RH) for 10,080 minutes. The amount of UV light the specimens were exposed to was 0.24 ± 0.01 W/m^2 for seven days. The different time intervals including 1, 3, 5 and 7 days were used to measure the resistance of UV, fading, and damages of the surface of the coating.

3.3.11 Thermal and water resistance test (Sweating Guarded Hotplate)

Thermal resistance can be measured in the process of heat and moisture transfer between the skin and the fabric. Heat resistance of coated and uncoated fabrics was measured three times on the sweating guarded hotplate (SDL Atlas Pty Ltd, England) using ISO11092:1993 (E) standard (Organization, 1993). Three specimens were cut into 30 x 30 cm of each fabric and precondition required at the standard environment at 20°C with 64% RH for twenty-four hours. Calibration was required for the bare plate and gets the three reading for standard temperature and humidity. After conditioning, the specimen was inserted on the measuring plate with face-up side. The heat leakage was controlled by using masking tape to cover all four sides of the specimen’s edge and remove all air bubbles or air gaps between the specimen surface and measuring plate. Thermal resistances were measured of the uncoated and coated fabrics in (dry condition) of each sample with three readings. Thermal resistances measured the energy required to maintain the constant temperature of 34°C of the measuring plate. So, the energy value is defining the temperature differences between the measuring plate surface and surrounding air circulation were used to determine the thermal resistances of fabric. Set temperature of measuring unit (T_m) was 34°C, air temperature (T_a) was 20°C and relative humidity (RH) was 64%, the air circulation speed was 1m/s. Thermal resistances were measured by using the formula was given below:

$$R_{ct} = \frac{(T_m - T_a).\ A - R_{cto}}{H - \Delta H_C}$$

Where

R_{ct} = Thermal resistances of fabric [m^2 K/W]

R_{cto} = Constant bare plate measurement of thermal resistances

A = Area of the surface of measuring plate in 0.03 m^2

T_a = Temperature of the air circulation in the chamber in degree Celsius

T_m = Temperature of the measuring plate in degree Celsius

H = Heating power supplied to the measuring unit in watts to maintain the temperature of measuring plate

ΔH_C = Heating power for the measurements of the thermal resistances R_{ct}

3.3.12 Water vapour resistance test

Water vapour resistance (R_{et}) is required to estimate the water vapour pressure of the top and bottom layer of the coated fabrics. Water vapour resistances of coated and uncoated fabrics were measured three times with the sweating guarded hot plate (SDL Atlas Pty Ltd, England) using the ISO11092: 1993 (E) standard (Organization, 1993). The required power was to maintain the temperature of measuring plate with 15 minutes. Test condition required to maintain the temperature of 34°C and humidity with 30% RH. During the test required the airspeed was circulation 1m/s in the chamber.

$$R_{et} = \frac{(p_m - p_a).\ A - R_{eto}}{H - \Delta H_e}$$

Where

R_{et} = Water vapour resistances of fabric [m^2 Pa / W]

R_{et0} = Constant bare plate measurement of water vapour resistances

A = Area of the surface of measuring plate in 0.03 m^2

p_a = water vapour partial pressure in Pascals at (T_a) Temperature of the air circulation in the chamber in degree Celsius

p_m = Saturation water vapour partial pressure in Pascals at (T_m) Temperature of the measuring plate in the chamber in degree Celsius

H = Heating power supplied to the measuring unit in watts and to maintain the temperature of measuring plate

ΔH_e = Heating power for the measurements of the water vapour resistance R_{et}

3.3.13 Moisture management properties (MMT)

The moisture management property of fabrics was measured on the SDL Atlas moisture management tester (MMT), in accordance with the standard AATCC-TM-195 (American Association of Textile Chemists and Colorists, 2012b). Five specimens 80 cm × 80 cm were prepared to do the test under the standard condition. A saline solution was penetrating from the top side to the bottom side of the sample in the test, while the wetting time, wetting radius, spreading time, absorption and overall moisture management capacity (OMMC) were reported on the associated computer.

3.3.14 Grab test

The mechanical properties of the coated fabric were measured on a tensile strength tester (INSTRON, USA) according to the ASTM 1682 Grab Test (American Society for Testing and Materials). Before testing, the coated fabrics were conditioning at 20 ± 2°C and 64 ± 2% RH for 4 hours. Samples with the size of 100 mm wide x 140 mm long were used and the central piece 24 mm of fabric was stressed. The fabric marked on both side of edge 37 mm and clamping between the jaws. The gauge length of coated fabrics was about 74 mm, and the speed was set at 20 ± 2 seconds. The central piece of fabric was under stress to measure the strength of fabrics.

3.3.15 Hydrostatic pressure test

Hydrostatic pressure tester (IDM Instrument Pty Ltd, Australia) was used to measure water resistance of the coated fabric in accordance with (Australia Standard, 1987). To carry out the test, the hydrostatic pressure was applied at three different points on the fabric to measure the leakage or resistance of water on the fabric. To conduct this, three fabric specimens of coated fabrics were cut in the size 200 mm x 200 mm. These specimens were then conditioned at 21 ± 2°C with 64 ± 2 RH for at least 4 hours before testing. After this these specimens were subjected to hydrostatic pressure in the range of 60-200 kPa.

3.3.16 Water repellency test

The Water repellency test (Toyoseiki, Tokyo, Japan) was performed in accordance with AATCC 22: 2010 to measure the water resistance of the coated fabrics (American Association of Textile Chemists and Colorists, 2014). Before testing, the coated fabrics were conditioning at 20 ± 2°C and 64 ± 2% RH for 4 hours. Samples with the size of 180 mm x180 mm were secured between the test hoops then 240 millilitre of distilled water was sprayed onto the surface of coated fabric over 30 seconds. Each sample was then spray rated using the international standard chart for spray rating, see Table 3-5.

Table 3-5: AATCC Standard spray test ratings.

Rating	**Description**
100 (ISO-4)	No wetting or non-sticking of the upper surface
90 (ISO-4)	Slightly random sticking or wetting surface at sprayed points
80 (ISO-3)	Wetting of the upper surface at sprayed points
70 (ISO-2)	Partial wetting of upper surface at sprayed points
50 (ISO-1)	Completed wetting of the sprayed surface
0	Wetting of the whole upper and lower surface at sprayed points

3.3.17 Oil repellency test

The oil repellency test was performed to measure the oil repellency of the coated fabric in accordance with AATCC 118: 2013 standard (American Association of Textile Chemists and Colorists, 2013c). Three specimens were cut in the size of 2 mm x 2 mm square and were placed in petri-dish. Three 10.0 microlitre drops of the chemicals were placed on the three-fabric specimen. Three types of oil, namely n-hexadecane, n-decane, and n-heptane, were used to do the test. The chemical droplets on the fabric were observed after 300 and 600 seconds at an angle of 34°. The grade was recorded if the droplet was repelled otherwise a zero was recorded if it penetrated into the fabric (Table 3-6). Grading of oil repellency which has been expressed to the nearest 0.5 indicates a borderline pass for the chemical test.

Table 3-6: AATCC Standard test oil liquids.

Oil repellency grade number	**Composition**	**Surface tension (dynes/cm)**
0	-	-
1	Mineral oil	31.5
2	64:34 Mineral oil: n-Hexadecane	-
3	n-Hexadecane	27. 3
4	n-Tetradecane	26. 4
5	n-Dodecane	24. 7
6	n-Decane	23. 4
7	n-Octane	21. 4
8	n-Heptane	19. 8

3.3.18 Aqueous liquids repellency test

Aqueous liquids repellency test was performed in accordance with the AATCC 193: 2012 standard. Three specimens were cut in the size of 2 mm x 2 mm square and were placed in a petri dish (American Association of Textile Chemists and Colorists, 2012a). Three droplets of the chemical (Isopropyl alcohol, 10 microlitre) were placed on the specimen. The chemical droplets on the fabric were observed after 300 and 600 seconds at an angle of 44°. The grade was recorded if the droplet was repelled otherwise a zero was recorded if it penetrated into the fabric (See Table 3-7). Grading of aqueous liquids repellency which has been expressed to the nearest 0.5 indicates a borderline pass for the chemical test.

Table 3-7: AATCC Standard aqueous liquids.

Aqueous repellency grade number	**Composition**	**Surface tension (dynes/cm)**
0	None (fail 98% Water)	-
1	98:2 Water: Isopropyl alcohol	49.0
2	94:5 Water: Isopropyl alcohol	40.0
3	90:10 Water: Isopropyl alcohol	32.0
4	80:20 Water: Isopropyl alcohol	33.0
5	70:30 Water: Isopropyl alcohol	27.4
6	60:30 Water: Isopropyl alcohol	24.3
7	40:40 Water: Isopropyl alcohol	23.4
8	30:60 Water: Isopropyl alcohol	23.0

3.3.19 Chemical resistance test

The chemical resistance testing method has been developed from the standard methods of American Society for Testing and Materials (ASTM). The specific issue of method requirements for chemical evaluation is explained in ASTM F1001-99 (a) for protective clothing (Forsberg, 2001). This test method is applicable only for liquid chemicals but not suitable for solvents. The list of chemicals is followed by the standard methods and the chemical resistance can be analysed with a modified method of oil repellency.

The chemical resistance of coated and uncoated fabric was evaluated using the similar method for the oil and aqueous liquids repellency testing. Three specimens were cut in the size of 2 mm x 2 mm and placed in a petri-dish. Three 10.0 microlitre drops of the chemicals were placed on each fabric specimens. Sixteen types of chemicals were used to do the test, and water was employed in the test for comparison. Photos of the droplets on the fabric were taken from an angle of 44° after 300 seconds and 600 seconds, respectively. The time for chemicals to diffuse into the sample was also recorded.

3.3.20 Soil release stain test

The soil resistance was measured with the stain on the fabrics, according to the standard method AATCC-130-2015 with the minor change of replacing oil (corn oil) with water (American Association of Textile Chemists and Colorists, 2016). Soil particles (5.0 g) were dissolved in 5.0 millilitre of water to make the solution. A medicine dropper was used to drop the solution onto the fabric surface. Three specimens with the size of 50 cm x 100 cm were used to determine the soil staining. The specimen was mounted on a glass slide at 45^o with the help of paper clips. Soil resistance was measured into five grades of equivalent staining for 20 seconds. The grade of soil resistance was rated by comparing the observed stain to the standard stains, with grade 5 the best soil resistance and grade 1 the worst soil resistance (see Table 3-8). A piece of white blotter paper was placed at the bottom to absorb the remaining solution of soil from the fabric surface.

Table 3-8: AATCC Standard soil release stain resistances.

Grading	Surface evaluation
5	Stain equivalent to standard stain 5
4	Stain equivalent to standard stain 4
3	Stain equivalent to standard stain 3
2	Stain equivalent to standard stain 2
1	Stain equivalent to standard stain 1

4 CHEMICAL AND WATER PROTECTIVE SURFACE ON COTTON FABRICS BY PAD-KNIFE-PAD COATING OF WPU-PDMS-TMS

4.1 Introduction

Surface functionalization of textiles is essential to protect different kinds of consumers from potential environmental hazards including hazardous liquid, poisonous chemical and biological contamination. Surface properties of clothing, such as water resistance, breathability, superhydrophobicity and stain resistance, are significant for military uniform and sportswear to withstand severe weather conditions while keeping hygienic and comfortable for wearers, and resist hazards imparted from chemicals, dirt, and soil, oil and water. Water repellent and moisture/air permeable fabric have been developed, in which the breathable or microspores membrane is used to generate resistance to water while allowing the penetration of air and water vapour (Borisova and Reihmane, 2013). As an example, the Gore-Tex® polytetrafluoroethylene (PTFE) membrane has been commercialised in textile industry. In addition, fluoro-based polymers or compound have been widely used in the textile industry to form hydrophobic surfaces that are not only repellent to water but also have good resistance to oil (Colleoni et al., 2015). These surfaces have low surface energy, exhibiting lotus effect or self-cleaning properties when subject to liquids. Fluoro-based polyurethane was used to form hydrophobic coatings, it formed short chains fluoro-alkyl such as $CF_3CF_2CH_2$ and $(CF_3)_2CH$ on cotton fabric (Jiang et al., 2006) even though the durability to washing was an issue. Polyurethane has also been used with methyl acrylate (MA) and fluoro-ethers such as perfluoro-alkyl ether acrylate to improve hydrophobic surface properties of the coating (Lim et al., 2001). However, the coating negatively altered thermal properties of the coated fabric (Zhu et al., 2008). Another compound used to develop superhydrophobic surface was polyurethane synthesized with perfluoro-octanate chains, this coating also imparted UV visible properties to the fabric (Liu et al., 2012). However, Fluoro-based polymers have the long chain of hydrocarbon that can break up into toxic compounds of perfluoro-octanoic acids (PFOA) and perfluoro-octane sulphonates (PFOS), which are extremely harmful to the human health and surrounding environment and thus are banned all over the world (Hekster et al., 2002).

Alternatively, eco-friendly non-fluorinated polymers such as polyurethane and silicone and its derivatives compound are commonly used in place of fluoro-based polymers to form the hydrophobic surface.

A mixture of hexadecyltrimethoxysilane (HDTMS), 3, 3glycidyloxypropyltrimethoxysilane (GTMS) and tetraethoxyorthosilicate (TEOS) with silica nanocomposite compounds was used to create a superhydrophobic surface on cotton fabrics with a contact angle of 141° and 104° after washing (Daoud et al., 2004). Bis (triethoxysilyl) ethane and octyltrimethoxysilane together with silica nanoparticles were also used to develop the superhydrophobic substrate with a contact angle of 139° on cotton fabric (Roe and Zhang, 2009). Fluorinated alkyl silane (FAS) was also grafted onto cotton and nylon blended substrates to explore high initial superhydrophobic and superoleophobic surfaces (Satam et al., 2010). In addition, fluorinated alkyl silane (FAS) and fluorinated-decyl polyhedral oligomeric silsesquioxane (FD-POSS) were used to produce water repellent coatings on the surface on polyester fabrics (Wang et al., 2011), but the abrasion resistance of the coated fabric was an issue. In addition, Polyurethane has been widely used as conductive polymer, wind and water proof breathable (Lomax, 2007) and flame retardant (Chen et al., 2005, Wu et al., 2014) materials, owing to its smooth surface, flexibility and soft hand, rigidity and strong physical properties, and safety to human and environment.

In combination with PDMS, polyurethane exhibits low glass transition point, low surface energy and excellent thermal stability (Pergal et al., 2013). PDMS has been successfully used with waterborne polyurethanes to achieve water proofing of clothing. A contact angle of 146° was achieved while the durability of the coating might be an issue. Polyurethane was combined with PDMS and 1H, 1H, 2H, 2H-perfluoro-1-octanol (PDMS/PFC) to produce the hydrophobic coating for biomedical applications, and the reduction of non-adherent properties of the coating was obvious at a contact angle of 118° (Butruk et al., 2011). Soy-based polyols of polyurethane, perfluoro-polyether, and PDMS were also combined in the form of a film to impart hydrophobicity and oleophobicity to steel panel while the mechanical properties were improved (Rengasamy and Mannari, 2013). Even though coating has been proved to be an effective way of functionalizing the surface of textiles, protective clothing usually needs to withstand different hazards from the environment including water, liquid, oil, and chemicals, and the durability of the coating must be excellent to justify further application of the coating technology. Thus, a versatile and durable coating with repellency to water/liquid, oil and chemicals are still of great challenge.

The durable functional coating on cotton fabric would bring opportunities to the development of cotton protective clothing; it has application potential in high performance and safety protective apparel.

This study explores the effects of WPU combined with various concentrations of PDMS/TMS on cotton fabric to enhance its repellent and hydrophobic properties. The aim of this research is to enhance multifunctional properties of cotton fabric by pad-batch/knife coating. Coating of WPU membrane acted as a waterproof barrier and PDMS/TMS acted as a repellent layer. WPU-PDMS/TMS coated fabric does not only have high contact angle but also is resistant to water oil and aqueous liquids solution. The developed coating method can be further applied in exploring protective clothing for military force and specialised workers who deal with hazardous chemicals and liquids.

4.2 Materials and Methods

4.2.1 Materials

Cotton fabric (plain, 150 g/m^2) was sourced from Bruck Textiles, Australia. ICB Fix Tubicoat Iso-cyanates and waterborne polyurethane (WPU, Tubicoat membrane 1665, in paste form) was purchased from CHT Pty Ltd, Australia. A mixture of 35% polydimethylsiloxane (PDMS) and 35% Trimethylated silica (TMS) were purchased from Dow Corning Pty Ltd, Australia. Hexadecane and n-Decane were obtained from Sigma Aldrich. Heptane (HPLC grade) was provided by RCL LAB SCAN Limited, Australia. Isopropyl alcohol (Ana-R) was purchased from BDH Limited Poole, England.

4.2.2 Pad-Knife-Pad coating

The cotton fabric was wetted by 0.01% (w/v) Triton X-100 solution in water for 30 minutes and scoured by caustic soda at 90°C for 1 hour. The fabric was rinsed with warm water and then with cold water, followed by an overnight hanging dry.

The scoured cotton fabric was subject to a three-step coating as illustrated in Figure 4-1. Firstly, Ernst Benz Pad was used to perform ICB Fix padding for three passages. The solution in the pad contained 0.15 g of ICB Fix dissolve in 30 ml of distilled water. The sample was dried at 60°C for 30 minutes. After padding, the percentage of the total pickup on the cotton fabric was calculated.

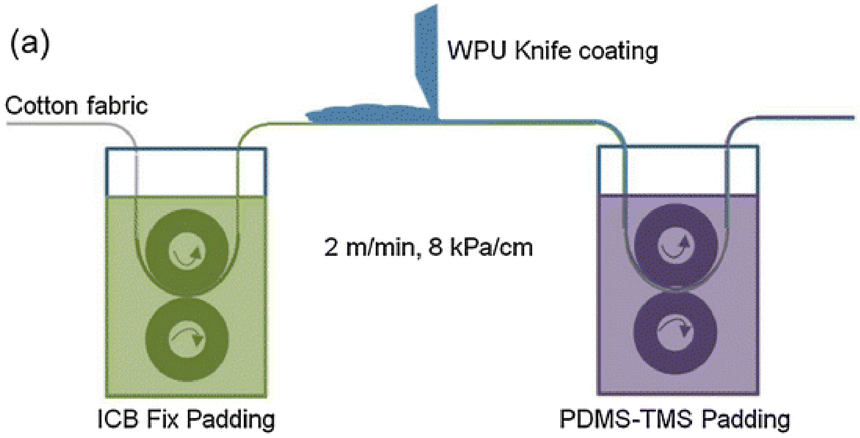

Figure 4-1: Pad-knife-pad coating of WPU-PDMS-TMS on cotton fabric.

Secondly, the padded fabric was coated with 30-44 g original paste of WPU membrane (Tubicoat 1665) by knife coating edge rollover method. The sample was dried at 60° C for 30 minutes. The thickness of WPU membrane coating was calculated on a thickness tester (British Indicators Ltd, St. Albans) according to AS 2001.2.14 method.

Thirdly, the pad-knife treated fabric was further padded with PDMS-TMS. The PDMS/TMS combined solution was diluted with n-Heptane with a concentration of 2%, 4%, 6% and 8%, respectively. The sample was dried at 60°C for 30 minutes followed by a 150°C curing process for 3 minutes. A three-layer coated ultra-hydrophobic surface was then formed on cotton fabric based on the copolymerization of WPU-PDMS/TMS (WPT).

4.3 Results and discussion

The study investigates effects of WPU as a suitable coating for cotton fabrics to impart chemical and water protective properties. WPU combined with PDMS/TMS was coated onto cotton fabric through the pad-knife-pad method; this initiated the copolymerization of WPU with PDMS/TMS. The wettability of cotton fabrics was greatly changed due to the formation of PDMS methyl long chains between the amino groups of WPU. The hydroxyl and amino groups of WPU are combined with PDMS to form different copolymers of polydimethylsiloxane diamines, which enhance the hardness, softness, and flexibility of the cotton fabric. WPU-PDMS/TMS provides flexible and soft segments with siloxane group which reduces the surface energy of cotton fabric (Wu et al., 2014).

4.3.1 FTIR spectra

Figure 4-2 illustrates the FTIR spectra of cotton (a), WPU coated only (b), PT coated only (c) and WPT coated (d-g) with the concentration of PT from 2 % to 8 %. Cotton fabric (Figure 4-2(a)) exhibits characteristic peaks around 3300, 2934, 1424, 1240 and 1072 cm^{-1} , corresponding for H-bonded OH stretching, CH_2 stretching, CH wagging, CH and C-O-C stretching, respectively.

Cotton fabric coated with WPU only (Figure 4-2(b)) shows the characteristic peaks for polyurethane, including the NH wagging bands at 770 cm^{-1}, CH stretching bands at 817 and 848 cm^{-1}. The absorption peaks at 1718 cm^{-1} are ascribed to C=O group of urea and urethane, and the peaks at 1444, 1431 and 1497 cm^{-1} owing to the benzene ring C=C group of WPU. The peaks of WPU membrane also indicates the presence of symmetric and asymmetric bands of CH_2 and CH_3 groups at around 2934 and 2681 cm^{-1}, respectively.

Cotton fabric coated with 8% PT only (Figure 4-2(c)) exhibits the absorption bands at around 799 cm^{-1} for $(CH_3)_2$-Si linkage. The absorption bands at around 1017, 1071 and 1087 cm^{-1} indicate the presence of Si-O-Si group and other bands at 1160 cm^{-1} for Si-O-C (Butruk et al., 2011, Pergal et al., 2013, Wu et al., 2014). The symmetric banding of Si-CH_3 can be seen at 1241 cm^{-1}, owing to the methyl groups of the TMS and PDMS.

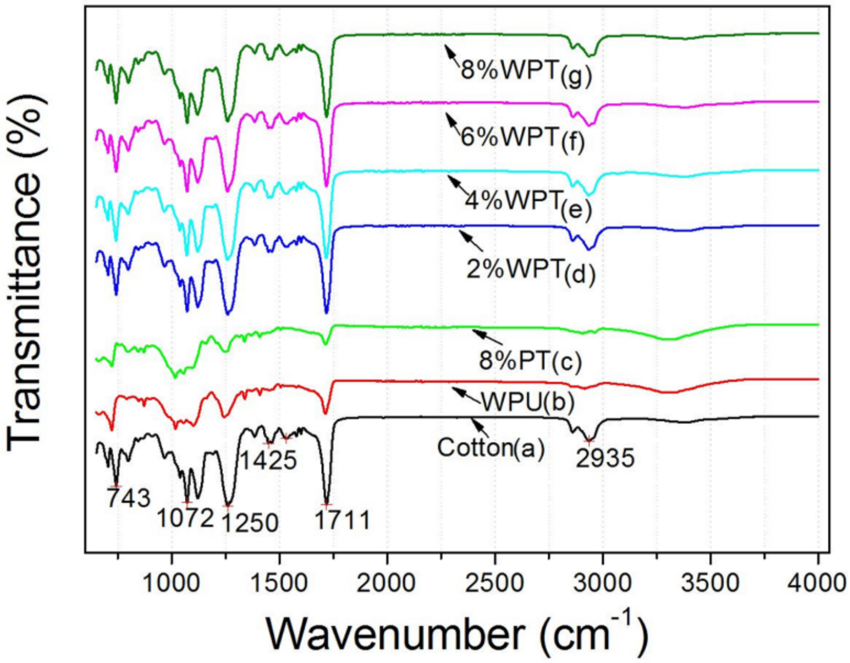

Figure 4-2: ATR-FTIR spectra of cotton, WPU coated only, 8% PT coated only and WPT coated with different concentrations of PT.

WPT coated fabric shows the characteristic peaks of WPU at 2935cm-^{1} and 1713 cm-^{1} for CH_2 and C=O group. In addition, the characteristic bands of PT such as the Si-O-Si and Si-O-C overlapped bands can be seen in all the spectra for WPT. These bands are more obvious with higher concentrations of PDMS. Similarly, the presence of TMS can be noted at 1251-1257 cm-^{1} and the peak becomes more evident with higher concentrations of PT. There is no difference in the absorption bands in the FTIR spectra of the 2-8% WPT coated.

4.3.2 SEM images

The uncoated cotton fabric shows a clear cellulose fibrous structure with different magnifications (100x, 400x and 1000x) in Figure 4-3 (1a-c).

After the coating with WPU membrane, the surface morphology of cotton fabrics changes with a thick membrane of WPU covering the cellulose fibres in Figure 4-3. 8% PT coated fabrics show rough surface on cotton fibres. WPTs in Figure 4-3 (4a-c) and the (7a-c) show the smooth WPU membrane at the bottom surface with a rough surface containing many white shiny particles from PT on the top layer. This enhances the ultra-hydrophobicity of the coated fabrics with the increase of the concentration of PT.

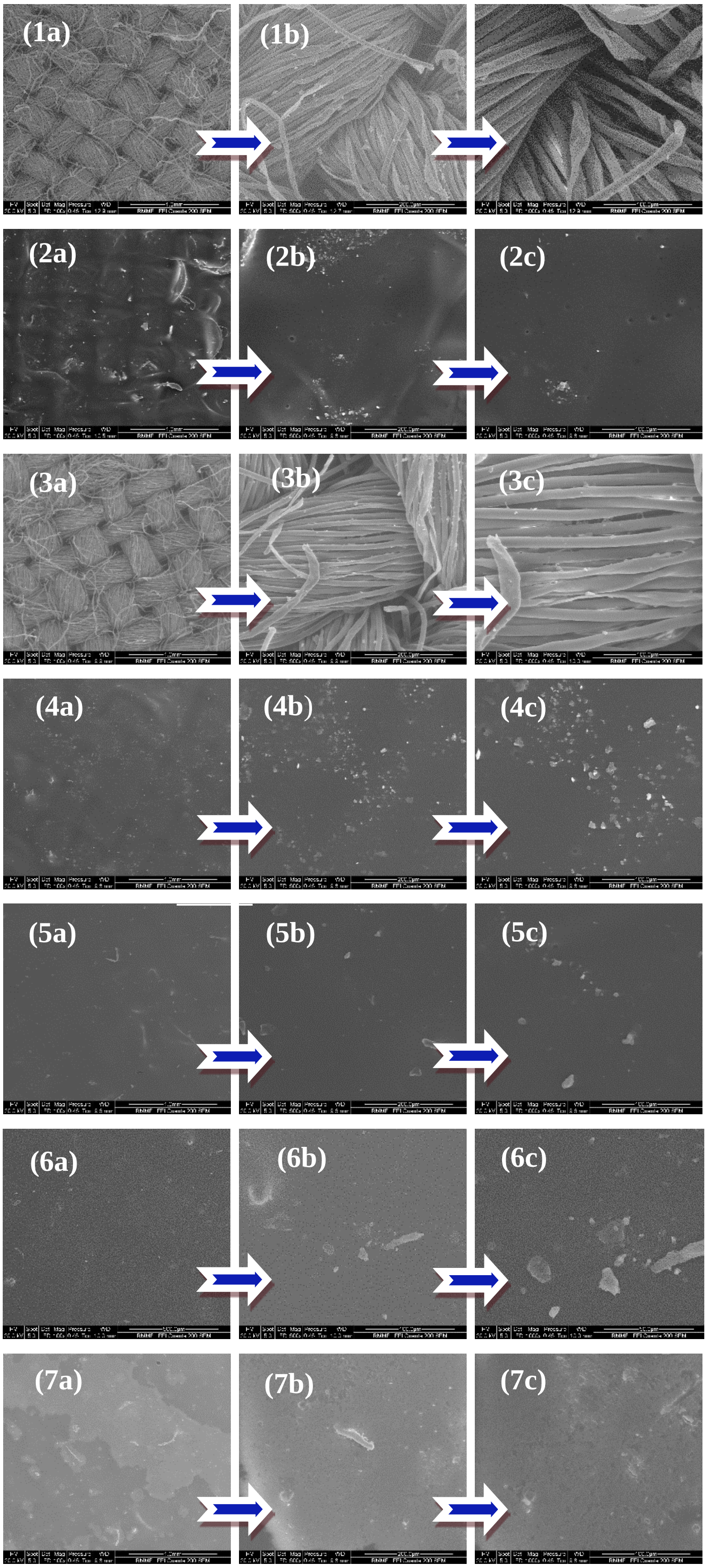

Figure 4-3: SEM images of uncoated (1), WPU (2), 8% PT (3), and 2-8 % WPT (4-7) coated fabrics at different magnifications (a = 100x, b = 400x, c = 1000x).

4.3.3 Contact angle

Pad-knife-pad coating has successfully brought waterproof properties to cotton fabric, as shown in Figure 4-4. Cotton fibre has a hydrophilic nature due to the hydroxyl groups in cellulose, and the CA of cotton fabric is around 30° WPU coated only cotton fabric gives a CA of 94°, suggesting that WPU membrane by itself provides ultra-hydrophobic and waterproof properties to the fabric to some level.

The reason for this is that WPU membrane increases the surface tension of cotton fabric to 72.8 dynes/cm. 8% PT coated only cotton fabric shows a CA of 155°, indicating a superhydrophobic surface of the coated cotton fabric. The high CA of the PT coating is due to the presence of polydimethylsiloxane group which reduces the surface energy of fabric (Chen et al., 2005).

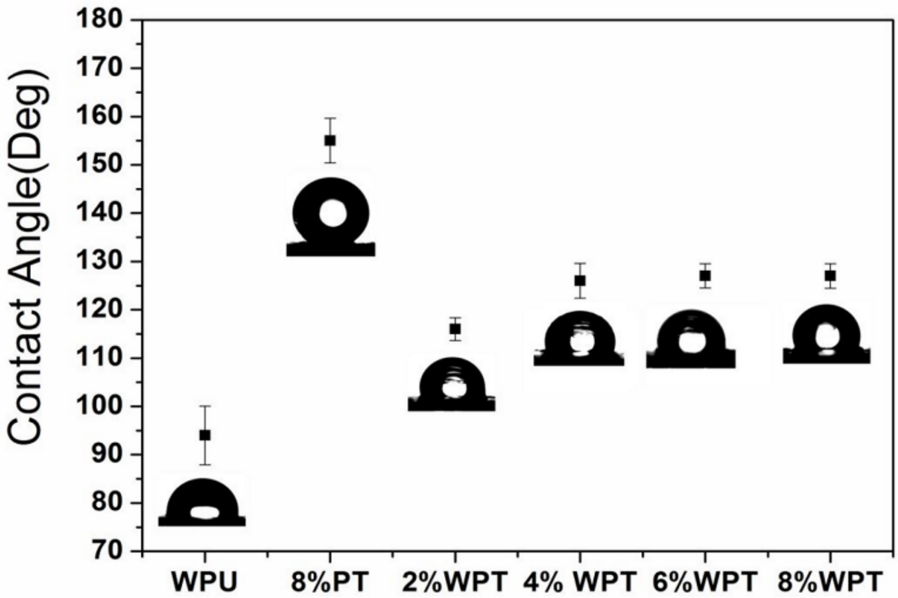

Figure 4-4: Contact angle of cotton fabric coated with WPU, 8% PT and WPT with different concentrations of PT.

WPT coated fabrics show lower contact angles than that of 8% PT but higher than WPU only, this is due to the existence of PT that further enhances the hydrophobicity of the WPU coated cotton fabric. With the increase of the concentration of PT, the CA increases slightly at first and then keeps stable as the high concentration of PT does not affect the already coated WPU further.

4.3.3 Durability of coating after laundering and crocking fastness

It is evident that WPT coating further enhances the water contact angle of WPU coating, resulting in higher water resistance properties to the coated cotton fabric. The water contact angle of cotton fabric is reduced evidently after laundering and crocking as shown in Figure 4-5. WPU coating shows very good durability as the water contact angle is the same after laundering and crocking. It is evident that the WPT coated cotton fabrics show excellent durability to laundering and crocking compared to that of uncoated cotton fabric as illustrated in Figure 4-5. The enhancement of durability of WPT coated fabrics is due to the copolymerization of WPU with PDMS-TMS by the formation of PDMS methyl long chains between the amino groups of WPU. It is thus obvious that WPT coating brings durable and water protective properties of cotton fabrics that show great application potential in protective clothing and safety apparel.

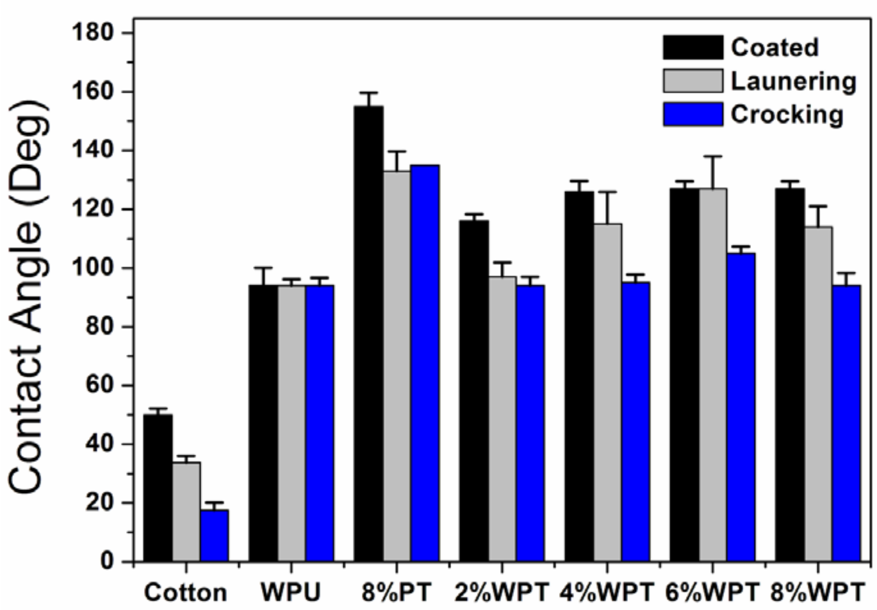

Figure 4-5: Contact angle of uncoated and coated fabrics after laundering and crocking to show the durability of coating.

4.3.4 Water repellency

In addition to CA that shows the surface wettability of materials, water repellency is a direct index for textiles to show waterproof properties. Water can be easily absorbed into cotton fabric due to the wettability of cotton fibre, so that the water repellency of cotton fabric is as low as 40%. WPU coated cotton fabric enhanced the water repellency to 70%, as shown in Figure 4-6.

The coated fabric is not absolutely repellent to water as some pores exist in the coated WPU membrane.

The 8% PT coated only cotton fabric has a water repellency of 100%, this is due to the siloxane group of PT that brings low surface energy to the fabric surface. In the WPT (Chen et al., 2005), which enhances the water repellency of WPU coated fabric to 80% and 90% for 2% WPT and 4% WPT, respectively. Further increase of PT concentration does not enhance the water repellency further as the bonding between the membrane and the PT solution stays the same after PT concentration reaches the threshold of 4%. Similar to the trend of water contact angle, the WPT coating further enhances the water repellency of WPU coating which would widen the application potential of the coated cotton fabric.

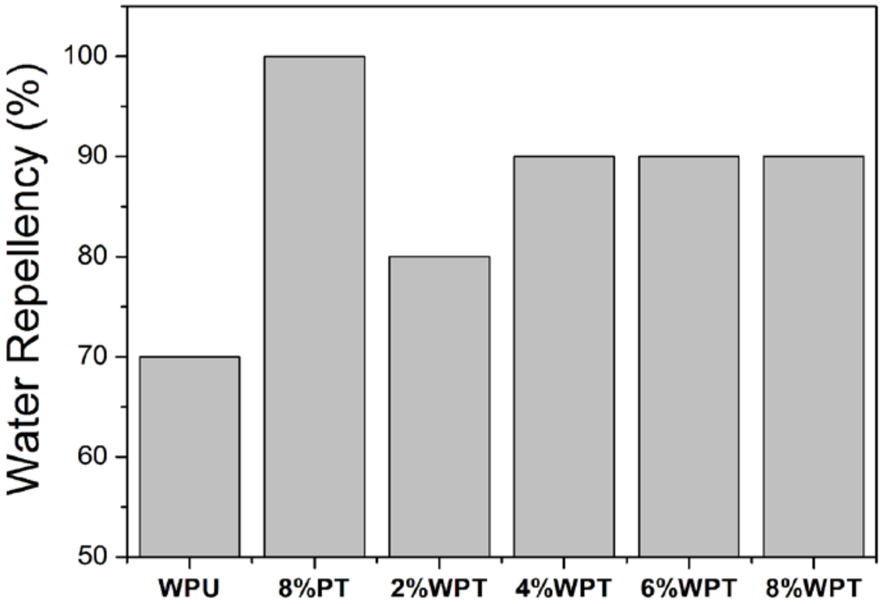

Figure 4-6: Water repellency of cotton fabric coated with WPU, 8% PT and WPT with different concentrations of PT.

4.3.5 Hydrostatic pressure

The hydrostatic pressure to water is a crucial index in protective clothing as the clothing is usually subject to liquid/water contact under different pressure. The level of hydrostatic pressure is thus important to protect the wearer and the higher the hydrostatic pressure, the better it will protect the wearer. However, the hydrostatic pressure for cotton fabric is zero kPa because of the wettability property of cotton fabric. Figure 4-7 shows the hydrostatic pressure of cotton fabric coated was different components by the pad-knife-pad method. WPU coated cotton fabric shows a hydrostatic pressure of 120 kPa, which significantly enhances the waterproof properties.

WPU membrane forms closed pores on the fabric surface, blocking water molecules from passing through under pressure. Hence, WPU acts as a water proof barrier to high hydrostatic pressure (Ozen, 2012).

However, the 8% PT coated only cotton fabric has a very low hydrostatic pressure of 1 kPa in comparison to WPU coated only one. The thin layer of PT coating on fabric consists of open pores, allowing water to pass through under pressure (Jassal et al., 2004). Therefore, when PT is applied without WPU, the coated fabric has poor resistance to hydrostatic pressure. Experimental observation reveals that the size of pores within PT increased with the increase of PT concentration, the fabric was thus less resistant to hydrostatic pressure of water.

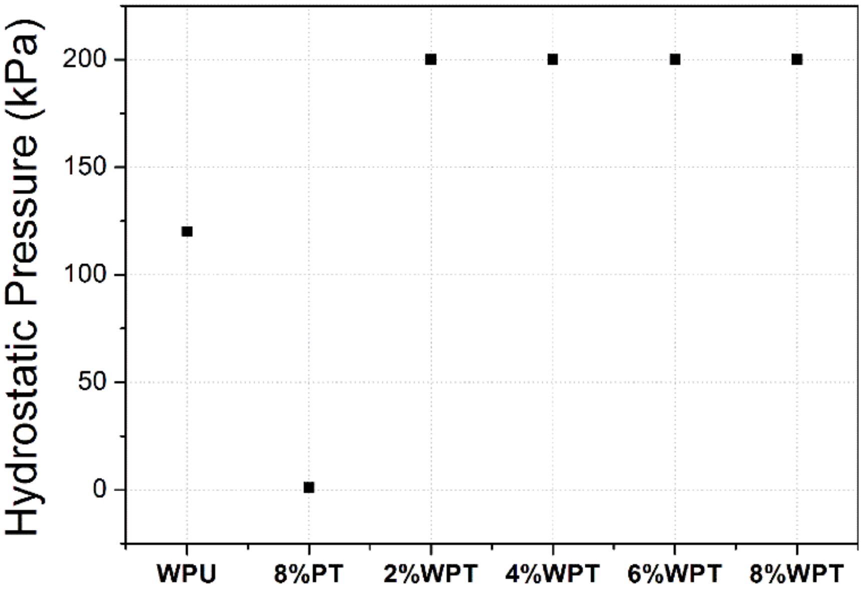

Figure 4-7: Hydrostatic pressure of cotton fabric coated with WPU, 8% PT and WPT with different concentrations of PT.

Cotton fabric coated with the combination of WPU and PT shows the excellent hydrostatic pressure of 200 kPa, as shown in Figure 4-7.

The surface of fabric becomes smooth and uniform without defects and open pores after adding the PT to WPU layer, making the coating a good barrier to liquids. Besides, the cross-linking and copolymerisation between WPU and PT on the surface result in higher strength against water pressure. It is noted that the hydrostatic pressure keeps stable at 200 kPa with the increase of PT concentration from 2% to 8%. Combined with the previously discussed water contact angle and water repellency, it is evident that WPT coating brings the coated cotton fabric with hydrophobicity, water repellency, and high hydrostatic pressure. This kind of versatile coating would prevent water from contacting, diffusion and penetration into clothing an application.

4.3.6 Oil repellency

The coated cotton fabric exhibits oil repellency compared with uncoated cotton, as shown in Figure 4-8. The WPU coated only shows good repellency to the n-heptane (blue droplet) as the WPU membrane builds high surface tension (72.8 dynes/cm) to prevent n-heptane from being absorbed into the fabric (Borisova and Reihmane, 2013, Vazquez, 2005, Wang et al., 2011).

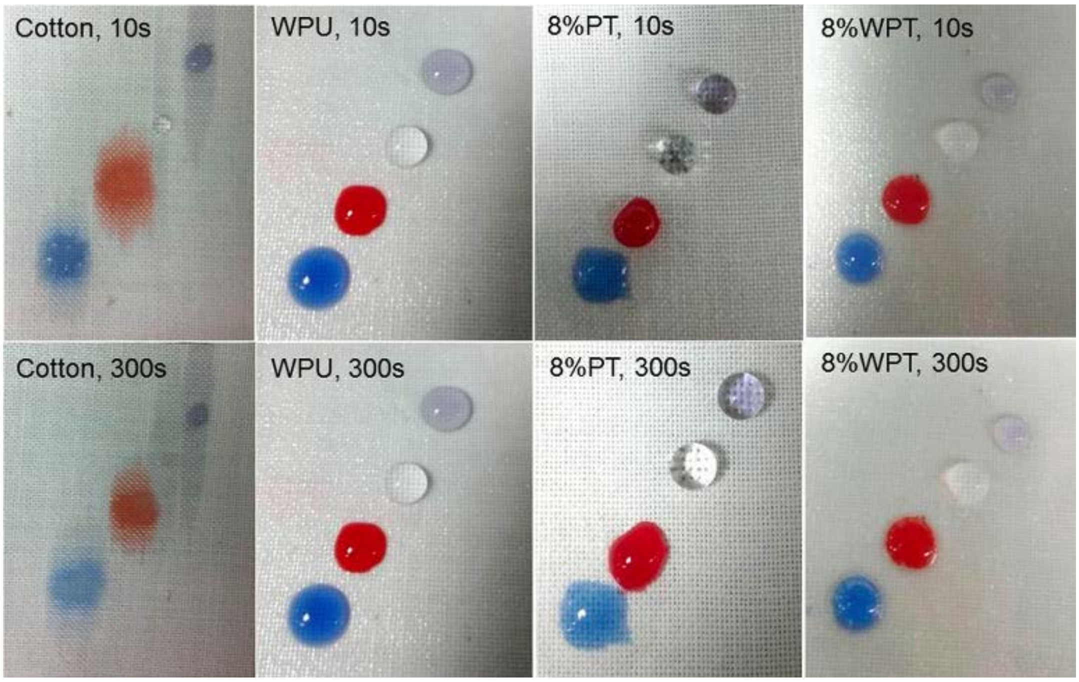

Figure 4-8: Oil repellency of uncoated, WPU coated only, 8% PT coated only and 8%WPT coated cotton fabrics (purple: n-Hexadecane; white: water; red: n-Decane; and blue: n-Heptane).

However, 8% PT coated only shows very poor repellency to n-heptane as the n-heptane hydrocarbon gets diluted in 8% PT solution and penetrates the coated fabric easily. The surface tension of 8% PT coated only (22.0 dynes/cm) is close to that of n-heptane (19.8 dynes/cm) and n-decane (23.8 dynes/cm), so that the red and blue droplets penetrate the fabric as shown in Figure 4-8. The purple droplet stays on the surface of 8% PT coated only without penetration due to its relatively higher surface tension (n-hexadecane, 27.3 dynes/cm) (Vazquez, 2005).

When WPU is combined with 8% PT, the surface tension of the fabric increases and hence the overall oil repellency is increased. It was noticed that when different concentrations of PT were further coated on the WPU fabric, the n-heptane droplet expanded in the top PT layer but not penetrated into the WPU layer. From the photos in, it is obvious that WPT coated fabric shows oil repellency to water and all kinds of oil.

4.3.7 Mechanical properties

It was also noted that WPU and WPT coated cotton fabric maintained the oil repellency and water resistance under tension (around 2 Newton load cell), however, 8% PT failed due to the fibrous structure of the cotton fabric. WPU has formed a smooth and intact membrane on the surface of the cotton fabric so that the protective properties were maintained under tension; this is very important to protective clothing as it will bear different tensions when the apparel is subject to different kinds of movements. It is evident that WPT coated cotton fabric has excellent oil repellency, which would benefit the application of protective clothing from cotton.

4.3.8 Aqueous liquid repellency

Cotton fabric is not resistant to aqueous liquid due to its excellent wettability. WPU coated only cotton fabric shows resistance to all the three types of aqueous liquid with different ratios of water/alcohol, as shown in Figure 4-9.

The surface of the aqueous liquid decreases from 44 dynes/cm to 33 dynes/cm and then 24 dynes/cm with the increase of the ratio of alcohol from 10% to 20% and then 40% in the liquid. The surface tension for 8% PT coated only fabric is 22 dynes/cm, so that the 60/40 liquid penetrates due to its closer surface tension to 8% PT. Whereas the 80/20 and 90/10 liquids with higher surface tension are repelled.

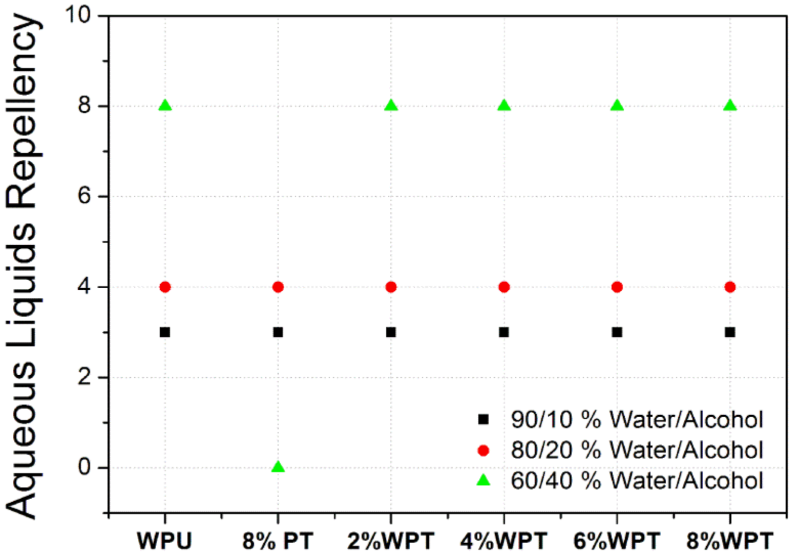

Figure 4-9: Aqueous liquids repellency grades of cotton fabric coated with WPU, 8% PT, and WPT with different concentrations of PT.

The combination of WPU and PT coating has excellent aqueous liquid repellency as the data for the WPT shown in Figure 4-9. It is evident that the WPT coated cotton fabric can withstand different aqueous liquids, resulting in a high application potential in protective clothing.

4.3.9 Chemical resistance

Table 4-1 lists the chemical resistance of the coated cotton fabrics to different chemicals. WPU coated shows better chemical resistance to 8% PT coated as the time for chemicals to diffuse into WPU coated is longer than that of 8% PT coated. WPT coated fabrics show higher chemical resistance than both WPU coated and 8% PT coated, and ten of the chemicals have been repelled successfully as shown in Table 4-1.

It takes longer time for other chemicals to diffuse into the WPT coated fabric (see Figure 4-10), suggesting an improved chemical resistance compared to WPU coated (Pan et al., 2012). It is evident that WPT coated cotton fabric repels most chemicals and thus this coating technology has great potential in developing chemical protective clothing.

Table 4-1: Chemical resistance (seconds) of cotton fabrics coated with WPU, 8% PT, and WPT with different concentrations of PT, ordered by surface tension.

Chemical	**Surface tension (dyne/cm)**	**WPU**	**8% PT**	**2% WPT**	**4% WPT**	**6% WPT**	**8% WPT**
n-Hexane	18.4	10	0	22	37	34	31
n-Heptane	19.8	300	0	300	300	300	300
Triethylamine	20.7	10	0	10	9	8	4
Methanol	22.1	247	0	300	300	300	300
Isopropyl alcohol	23.0	300	10	300	300	300	300
Acetone	23.2	49	10	81	99	116	129
n-Decane	23.8	300	0	300	300	300	300
n-Hexadecane	24.3	300	300	300	300	300	300
Paraffin oil	26.0	300	16	300	300	300	300
Tetrahydrofuran	26.4	62	0	111	100	80	70
Dichloromethane	26.8	14	4	14	20	22	24
n-Hexadecane	27.3	300	300	300	300	300	300
Acetic acid	27.0	300	300	300	300	300	300
Toluene	28.4	300	0	287	247	194	104
Acetonitrile	28.7	223	0	283	270	290	300
Dimethylformamide	36.7	300	300	300	300	300	300
Butadiene	47.0	300	300	300	300	300	300
Sulphuric acid	84.0	300	10	300	300	300	300
Sodium hydroxide	101.0	300	300	300	300	300	300

Figure 4-10: Chemical resistance after 300 second for coated fabric of 8% WPT and uncoated cotton fabrics.

4.3.10 Air permeability

The air permeability of untreated cotton fabric was 95.0 cm/s as airflow can easily penetrate through the pores of the fabric. The air permeability depends upon the pore sizes of fabric (Fang et al., 2012, Jassal et al., 2004, Kang et al., 2007, Zeng et al., 2015). The presence of WPU membrane affects the pore size and blocks the pores of fabric, thus the air permeability of WPU coated only drops dramatically to 0.184 cm/s (see Figure 4-11).

The reductions in the air permeability with the increase in hydrophobicity suggest a continuous defect-free film of WPU coating. 8% PT coated only shows higher air permeability than WPU as

PT coating does not affect the pore size of fabric. WPT coated fabric shows further lower air permeability than WPU and the permeability decreases with the increase of PT concentration.

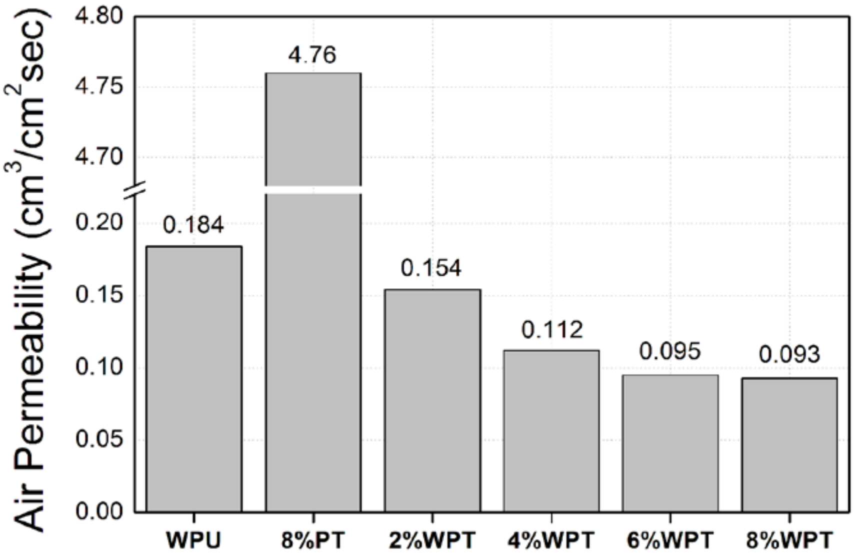

Figure 4-11: Air permeability flow rate of cotton fabrics of WPU membrane with different concentration of PT.

4.3.11 Ultraviolet resistance

Ultraviolet radiation exposure is a very important factor to describe the damaged surface of the hydrophobic coating. After exposure to UV radiation, the coating can be damaged due to the absorption of UV lights. Ultraviolet radiation exposure in Australia is very strong because the ozone layer has been destroyed to leak UV radiation. Firefighter protective clothing can block 94% of ultraviolet radiation, however, the tear and tensile strength and water repellency of the coating drop dramatically after exposure to UV for 13 days (Davis et al., 2010).

An ultraviolet curable method was applied on waterborne polyurethanes and PDMS to improve the functionality of coating and mechanical strength (Hwang et al., 2011). It has been found in this research that the hydrophobicity keeps at a satisfactory level after the high-intensity ultraviolet radiation exposure (40.32 kJ/m^2) of seven days, with a slight reduction of 3-4° in the CA (Figure 4-12). The damage of coating for 8% PT and 8%WPT was quite evident after the exposure to the reduction in CA was 24-12°. WPU membrane combining with repellent (2-6% PT) showed the excellent performance against ultraviolet radiation exposure.

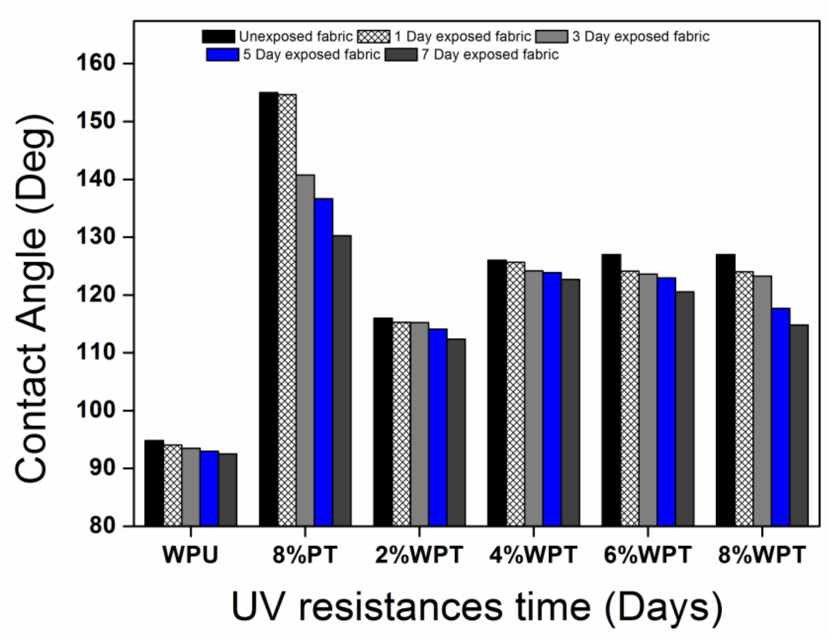

Figure 4-12: UV resistance of WPU, PT and WPT with different concentration of PT.

4.4 Summary

Ultra-hydrophobic coating on cotton fabric successfully provided multiple protective layers from waterborne polyurethane (WPU), polydimethylsiloxane (PDMS) and trimethylated silica (TMS). The chain of PDMS-TMS cross-linked and combined with the backbone chain of WPU membrane in the pad-knife-pad coating, initiating the copolymerization between the two polymers on the surface of the cotton fabric. A membrane with particles on the surface was formed on the WPT coated fabrics as observed from SEM photos. 8% PT coated cotton fabric showed a water contact angle of 155°, suggesting a hydrophobic surface on cotton fabric. The coating showed excellent durability after laundering and crocking. A combination of WPU-PDMS-TMS (WPT) coating on cotton fabric greatly enhanced the repellency and protective properties. The WPT coated fabric showed excellent repellency to water, oil, aqueous liquid and hydrostatic pressure. WPT coated cotton fabric also showed better chemical resistance than WPU coated and 8% PT coated, successfully repelled most chemicals and the time for other chemicals to diffuse into the coated fabric was much longer than WPU. After exposure to high-intensity ultraviolet light for seven days, the WPT coated fabrics showed the excellent hydrophobicity. The continuous defect-free WPU film on the surface of cotton fabric affected the pore size and blocked the pores of fabric, thus the air permeability of WPT coated cotton fabric was much lower than that of cotton fabric.

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5 COATING OF TPU-PDMS-TMS ON COTTON FABRICS FOR VERSATILE PROTECTION

5.1 Introduction

A coating is a very effective technology that brings extra functions to the substrate materials. A classic example of this is the coating for superhydrophobicity towards self-cleaning textiles, in which the superhydrophobic surface is measured by a water contact angle of >150° (Pan et al., 2012). Usually, for self-cleaning textiles, the apparent contact angle is very high (150–170°) and the angle of hysteresis is very low for the water droplets to roll off from the surface of the fabrics. Similar to hydrophobicity, oleophobicity has been developed to bring resistance against oils to fabrics. Chemical resistance is another important factor for protective clothing, and it is very effective in surface decontamination for military uniforms, mining clothing and outdoor sportswear (Gorzkowska-Sobas, 2013). When the surface of textiles is not penetrated by water, oils, and liquids chemicals (such as acids, base, and solvents), it is called omniphobic surface. The omniphobic surface of clothing is helpful in protecting skin against hazardous liquid chemicals, industrial chemicals, petroleum oils, lubricants and bacterial viruses. Versatile protection from the developed omniphobic surface of textiles is crucial for customers who are facing threats from either environment or working places.

Comfort is another important factor for developing protective clothing, as the widely applied coatings usually affect the thermal and moisture behaviour of the fabrics (especially their breathability which will severely deteriorate due to the blocking of pores in the fabrics).

Polytetrafluoroethylene (PTFE) has been used to develop protective textiles under the brand Gore-Tex$^{®}$. With a water contact angle of 110°, Gore-Tex has the properties of waterproof, breathability and windproof that make it applicable in various areas. The success of Gore-Tex indicates that a balance between protection and comfort is the key to developing the protective textiles. Besides, fluoro-based polymers or compounds have been widely applied to form superhydrophobic surfaces (Jiang et al., 2006, Lim et al., 2001). However, toxic by-products, such as perfluoro-octanoic acids (PFOA) and perfluorooctane sulphonates (PFOS), are usually produced in the synthesis of C_8-based fluorocarbon resins, and removal of them would result in high costs. Replacement of fluoro-based polymers for protective coating on fabrics is of great interests to textile industry (Hekster et al., 2002). Eco-friendly polymers have been developed to be the ideal replacement in this regard (Daoud et al., 2004). Among them, polyurethane and silicone together with its derivative compounds are promising in developing superhydrophobic surfaces on fabrics towards versatile protective clothing (Satam et al., 2010, Roe and Zhang, 2009). Polyurethane (PU) has been widely applied as coating materials for breathable but wind and water proof membranes (Lomax, 2007), and as flame retardant materials for functional textiles (Chen et al., 2005, Wu et al., 2014). The thermoplastic polyurethane (TPU) based materials have found to be suitable for protective textiles such as facemasks which resist chemical warfare agents (CWA) (Forsberg, 2001). Microporous PU membrane with self-decontaminating agent (polyoxometalate) was used for decontaminating the G-agent and distilled mustard (HD) surrogates (Walker et al., 2003). With good membrane-forming ability, polyurethane itself can provide protection to textiles. However, the surface of polyurethane would need further functionalization to introduce value-added protection mechanisms. A laminated coating of microporous PU membrane with polytetrafluoroethylene (PTFE) was used to form water and vapour resistant fabrics for sportswear (Jeong and An, 2001). Waterproof-breathable PU nanofibres coating has been used as high-performance protective clothing for sportswear industry (Romaškevič et al., 2006, Kang et al., 2007). As an environmentally friendly polymer, PU has been modified by 5, 5-dimethylhydantoin to form multifunctional and self-decontaminating biocidal surface to remove the gram positive and negative bacteria (Boileau et al., 2009, Makal et al., 2006).

In order to develop versatile protection against different agents, PU has been combined with other protection mechanisms to enhance the protection capacity. Recent research on polydimethylsiloxane (PDMS)-based silica surface or silica-based polymer surface has shown oil-water separation and versatile protection (Pergal et al., 2013, Rengasamy and Mannari, 2013, Moiz et al., 2016). Waterborne polyurethane was combined with PDMS-TMS to produce a hydrophobic surface with low surface tension and high resistance to water, oil, and chemicals. The chemical resistance to methanol, acetone and isopropyl alcohol requires a low surface tension of around 25 dynes/cm. Superoleophobic surface usually has a surface tension of less than 20 dynes/cm (Arkles, 2006), while superhydrophobic surface usually has a high surface tension of 72 dynes/cm (Borisova and Reihmane, 2013). It would be very challenging to achieve a superomniphobic surface that is resistant to water, oil, and chemicals in terms of reaching a compromised surface tension of the coated surface. A combination of waterborne polyurethane (WPU) cross-linked with PDMS and trimethylated silica (TMS) has been developed for this purpose to resist different agents including water, oil and chemicals (Moiz et al., 2016). However, due to the existence of the uniform membrane of WPU, the comfort, handle and flexibility of the coated cotton fabrics have been severely affected. It is a big challenge to develop versatile protective coating while maintaining the proper comfort of fabrics. Changes in the polyurethane, either its chemical composition or its structure, are needed for further development of polyurethane based versatile protective clothing.

A soft, flexible and protective coating that does not compromise much of the breathability of fabric structure is needed to address the challenge. It is thus important to study the substrate materials of polyurethane, and an ideal substrate would facilitate the functional coating while maintaining the comfort the as-coated fabrics. This study investigates the coating of thermoplastic polyurethane (TPU) combining with polydimethylsiloxane and trimethylated silica (PT) using a three-step pad-knife-pad coating on polycotton (PC) fabrics. A three-layered hierarchical structure based on the complex modification of TPU by PT has been obtained to form cross-linking reaction, in which the polydimethylsiloxane reacts with the amino groups of the polyurethane to form Si–OCH_3 compounds. The TPU-PDMS-TMS coating has shown higher hydrophobicity with better durability, more flexible handle and better thermophysiological comfort compared to the WPU-PDMS-TMS coating. This study will benefit the development of alternative coating processes to replace the fluoro-polymers based coating technology.

5.2 Experimental

5.2.1 Materials

Blended fabrics polycotton (150 g/m^2, plain) were purchased from Bruck Textiles, Abbotsford, Australia. The fabrics were fabricated from cotton and polyester fibres with a blend ratio of 80/20 for cotton/polyester, respectively. Tubicoat Fix ICB concentration was provided by CHT

Australia Pty Ltd., Dandenong South, Australia. Thermoplastic polyurethane (TPU, Texalan-598-A, in pellets form) were purchased from Pacific Urethanes Pty Ltd., Carrum Downs, Australia. Xiameter FBL-0563 (15–35% PDMS, 15–35% TMS) was sourced from Dow Corning Pty Ltd., Pennant Hills, Australia. Hexadecane and n-Decane were purchased from Sigma Aldrich Pty Ltd., Castle Hill, Australia. Heptane (HPLC grade) was purchased from RCL LAB SCAN Limited, Australia. Isopropyl alcohol (Ana-R) was purchased from BDH Limited, Dorset, UK. N, N-dimethylformamide (DMF) was purchased from Merck KGaA, Darmstadt, Germany.

5.2.2 Methods

The polycotton fabric was wetted by 0.01% (w/v) Triton X-100 solution in water for 30 minutes and scoured by caustic soda at 90°C for 1 hour. The fabric was rinsed with warm water and then with cold water, followed by an overnight hanging dry.

The polycotton fabric was then subject to a three-step coating process as illustrated in Figure 5-1. Firstly, an Ernst Benz Pad was used to perform ICB Fix padding for three passages. The solution in the pad contained 30 ml distilled water with 0.15 g ICB Fix dissolved in it. The fabric was first dipped into the solution to reach thorough impregnation. The fabric with solution impregnated was then passed between the two rollers of the pad to squeeze out air and to force the solution into the fabric.

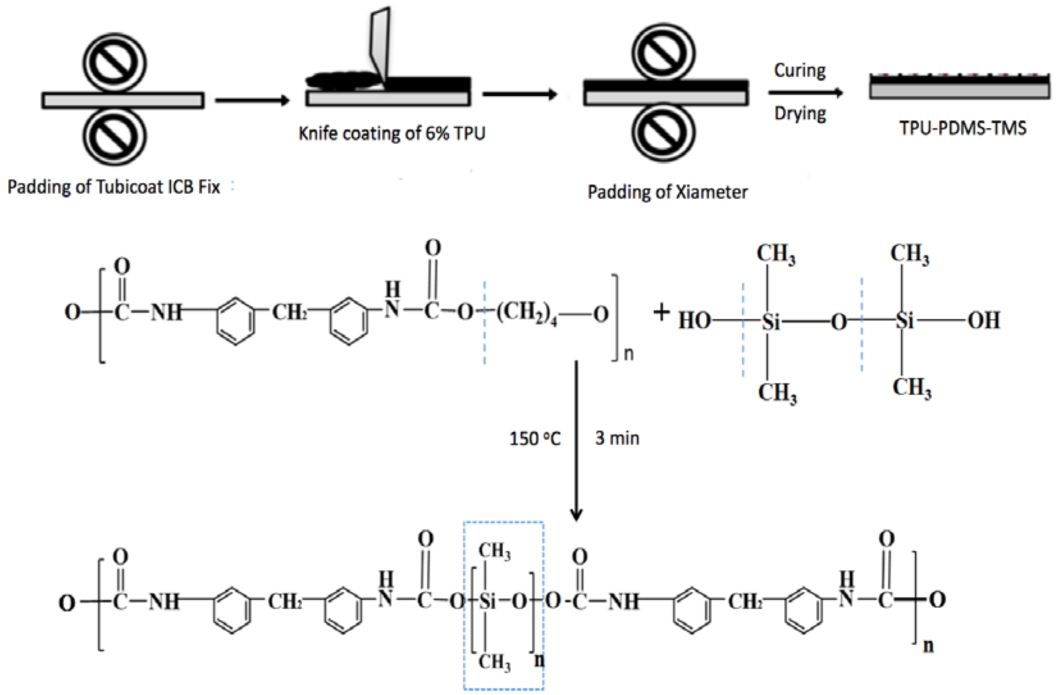

Figure 5-1: Schematics of pad-knife-pad coating of thermoplastic polyurethane (TPU)-polydimethylsiloxane (PDMS)-trimethylated silica (TMS) (TPT) on polycotton fabrics and the cross-linking mechanism.

The excess of the solution was sent back along the fabric to the solution bath at the same time. After this dip-nip process, the sample was dried at 60°C for 30 minutes and the percentage of the total pickup on the fabric was calculated.

Secondly, the padded fabric was coated with 6% TPU paste (prepared by dissolving TPU pellets in DMF) by a knife edge rolling over method. In the coating process, the fabric was mounted on the frame of the coater (Werner Mathis AG, Oberhasli, Switzerland), and the knife was set on the surface of the fabric with a given distance to determine the thickness of the coating. A certain amount of TPU paste was poured in front of the edge of the knife, and the knife was then moving slowly on the surface of the fabric to spread the TPU paste evenly. The thickness of the coating can be controlled by adjusting the distance between the knife edge and the fabric. The coated sample was then dried at 60°C for 30 minutes. The thickness of TPU coating was calculated on a thickness tester (British Indicators Ltd., St. Albans, UK) according to the AS 2001.2.14 methods.

Thirdly, the padded and knife coated fabric (6% TPU) was further padded with a PDMS-TMS solution. The PT solution was prepared by diluting the Xiameter FBL-0563 into n-heptane with the concentration of 2, 4, 6 and 8%, respectively. After padding, the sample was dried in a lab oven (Electrolux) at 60°C for 30 minutes. The sample was then placed in a curing unit (W. Mathis AG, Oberhasli, Switzerland) at 150°C for 3 minutes. The three-layered functional coating was then formed on the polycotton fabric based on the cross-linking network of TPU-PDMS-TMS (TPT).

5.3 Results and discussion

5.3.1 Characterizations

The combined coating of TPU and PDMS-TMS results in a cross-linked network on the surface of polycotton fabrics, and the network brings versatile protection to the fabrics. Tubicoat ICB Fix acts as the cross-linking agent that binds the TPU with polycotton fabrics, providing a durable and flexible substrate for forming cross-linked network. The cross-linking between TPU and PDMS-TMS is schematically depicted in Figure 5-1. The long chain of TPU combines with PDMS-TMS to form cross-linking, providing flexible and soft segments with siloxane groups to exhibit low surface energy on polycotton fabrics (Moiz et al., 2016, Wu et al., 2014). The handle test has found that all the coated polycotton fabrics are stiffer, less soft, and shiny in luster with lower bending ability than the uncoated polycotton fabrics. Nevertheless, the TPT coated fabrics are softer and more flexible than the previously developed WPU-PDMS-TMS (WPT) coated fabrics, suggesting improved handle property by adopting TPU rather than WPU.

5.3.1.1 FTIR spectra

The chemical components of coated fabrics were characterized by using FTIR-ATR spectroscopy, as shown in Figure 5-2. The spectrum of the uncoated polycotton shows significant bands around 3282, 2917, 1425, 1315, 1054 and 1017 cm^{-1}. These bands are due to the O-H vibration stretching, the CH_2 stretching, the CH bending, the asymmetric stretching of C-O-C, and the asymmetric plain stretching of C-O, respectively. The spectrum of TPU coated cotton fabric shows extra characteristic bands of urea and urethane groups, such as NH stretching band at around 3335 cm-^{1}, 2955 cm-^{1} for CH_2, and 1728 cm-^{1} for C=O. Besides, there are other relevant bands of benzene ring structure of TPU including 1597, 1531, 1454, and 1414 cm-^{1}.

The CH stretching bands can be observed around 848, and 817 cm-^{1} and the NH wagging bands can be identified by 770, 711, and 663cm^{-1} band. The 8% PT coated cotton fabric exhibits symmetric banding of TMS including the band at 1251cm^{-1} for Si-CH_3 and 1160cm^{-1} for Si-O-C. In addition, the vibration symmetric stretching bands of Si-O-Si can be observed around 1059, 876, 845 and 770 cm^{-1}.

The chemical components of the coated fabrics were characterized using FTIR-ATR spectroscopy, as shown the spectra in Figure 5-2. All the functional groups of the samples from the FTIR spectra are listed in Table 5-1. The spectrum of the uncoated polycotton fabric shows significant bands around 3282, 2917, 1425, 1315, 1054 and 1017 cm^{-1}. These bands are attributed to the O–H vibration stretching, the CH_2 stretching, the CH bending, the asymmetric stretching of C–O–C, and the asymmetric plain stretching of C–O, respectively.

The spectrum of TPU coated polycotton fabric shows characteristic bands of urethane groups, such as NH stretching band at around 3335, 2955 cm^{-1} for CH_2, and 1728 cm^{-1} for C=O. Besides, there are other relevant bands of the benzene ring structure of TPU including 1597, 1531, 1454, and 1414 cm^{-1}. The CH stretching bands can be observed around 848 and 817 cm^{-1}, and the NH wagging bands can be identified by the 770, 711, and 663 cm^{-1} bands.

The 8% PT coated polycotton fabric exhibits the symmetric banding of TMS including the bands at 1251 cm^{-1} for Si–CH_3 and at 1160 cm^{-1} for Si–O–C. In addition, the vibration symmetric stretching bands of Si–O–Si can be observed around 1059, 876, 845 and 770 cm^{-1}.

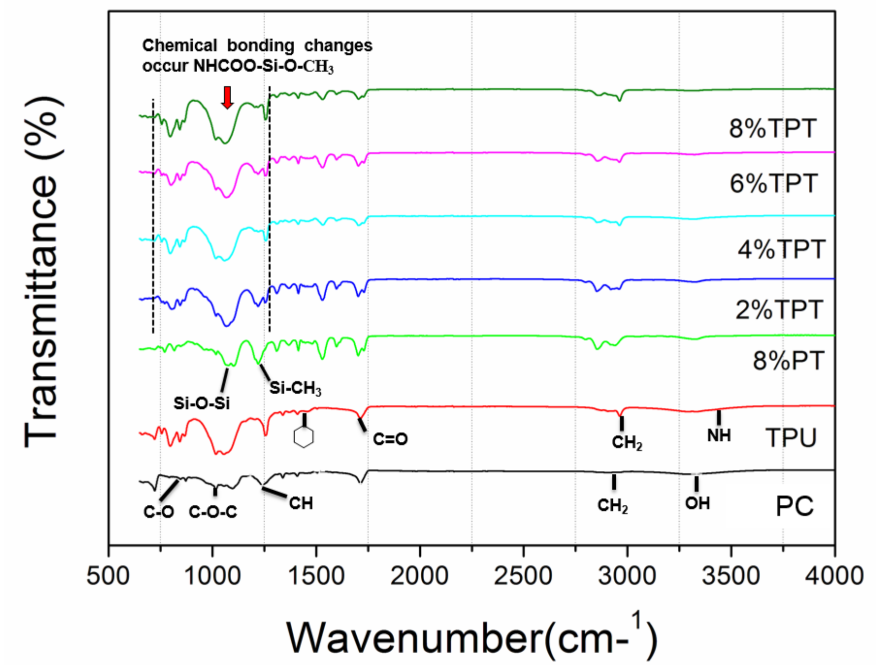

Figure 5-2: ATR-FTIR spectra of cotton, TPT coated only, 8%PT coated only and TPT with different concentration of PT.

Table 5-1: Detection functional groups for all coated and uncoated fabric by FTIR.

Samples	**Functional groups**	**Wave number (cm^{-1})**	**Attributed to**
Polycotton	O–H	3382 (v)	Stretching of hydroxyl group
	CH_2	2970 (vs)	Stretching of methyl group
	CH	1425 (δ)	Bending of methyl group
	C–O–C	1315 (a)	Asymmetric stretching of ester group
	C–O	1017 (a)	Asymmetric stretching of carbon monoxide group
TPU	NH	3335 (v)	Stretching of amide group
	CH_2	2955 (va)	Symmetric stretching of methyl group
	C=O	1728	Stretching of carbonyl group
	C=C Benzene ring	1597–1414 (δs)	Bending of symmetric of carbon with double bonding in ring
PDMS-TMS	CH_2	2975 (a)	Asymmetric stretching of methyl group
	$Si–CH_3$	1270–1250 (va)	Asymmetric stretching of methyl and silicone group
	$Si–(CH_3)_n$	870–700 (δ)	Bending stretching of silicone and no methyl groups
	Si–O–Si	1059–1020 (va)	Asymmetric stretching of silicones and oxygen group
TPU-PDMS-TMS	$NHCOO–Si–O–CH_3$	1713–749	Cross-linking between TPU chain and PDMS-TMS groups

Note: v: stretching, δ: bending, ρ: rocking, a: asymmetric and s: symmetric.

The TPT-coated polycotton fabrics with different PT concentrations show the characteristic bands of both TPU and PT. It is noted that the stretching bands at around 1713 to 749 cm^{-1} are ascribed to the cross-linking of TPU and PDMS-TMS (Wu et al., 2014, Chen et al., 2005). The spectra of TPTs show similar absorption bands, and the characteristic bands of PT are more evident with the increase of the concentration of PT. Specifically, the band intensity of Si–O–Si and $Si–CH_3$ increases gradually with the increase of PT concentration.

5.3.1.2 SEM photos

The coating has affected the morphology of polycotton fabrics, as indicated in Figure 5-3. The uncoated polycotton fabric shows a clear fibrous structure with the typical convolutional ribbon profiles of cotton fibres. The inset of Figure 5-3(a) shows the clean surface of a cotton fibre from the uncoated polycotton fabric.

TPU coating has brought a thin layer to the surface of fibres with neighbouring fibres bridging together, resulting in a rather smooth surface morphology as shown in Figure 5-3(b). Detailed view (the inset of Figure 5-3(b)) suggests that fibre has been coated successfully. Besides, the fibres have been bridged together as the gaps between neighbouring fibres are fed with TPU. Considering single fibres can be seen from the TPU-coated polycotton fabric, TPU coating hasn’t formed a bulky and uniform membrane on the fabric surface. 8% PT padding has hardly affected the morphology of polycotton fabrics but small shiny particles can be observed from the surface of fibres (the inset of Figure 5-3(c)). The TPT coating has brought a thin coating layer onto the surface of fibres with particles on it, as shown in Figure 5-3(d-f). More particles can be observed with the increase of the concentration of PT, as seen from the insets. The previous study on waterborne polyurethane coating (Moiz et al., 2016) indicated that a uniform membrane was formed to cover the surface of the cotton fabrics. It can be seen from the SEM photos that the fibrous structure of polycotton fabrics has been partly preserved after TPT coating, and the particles contribute to the surface roughness of the coated polycotton fabric.

5.3.2 Versatile protection

5.3.2.1 Water contact angle

The coating of TPU-PDMS-TMS has brought protection against water to polycotton fabrics. Figure 5-4 shows the water contact angle of polycotton fabrics before and after coating.

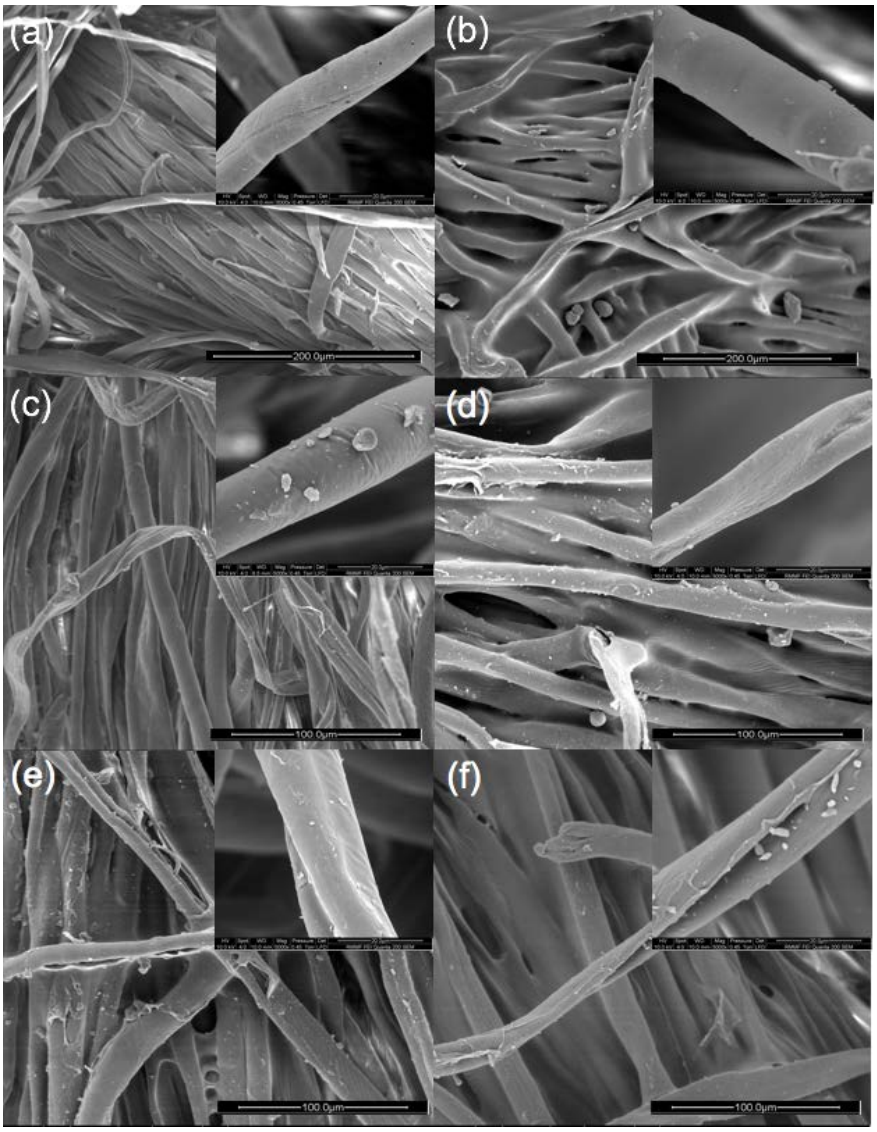

Figure 5-3: Scanning electron microscopy (SEM) photos of (a) uncoated polycotton fabric; (b) TPU coated; (c) 8% PT coated; (d) 2% TPT coated; (e) 4% TPT coated; and (f) 6% TPT coated (Insets: detailed view with scale bar 20µm).

Untreated polycotton fabrics have very good wettability to water with an immediate water contact angle of around 50°, and no evident water contact angle can be observed after one minute as the droplet will be absorbed into the fabric. A simple knife coating of TPU has resulted in an enhancement of water contact angle to 134 ± 10° with hysteresis of 4.61 ± 2°, indicating that a hydrophobic surface has been formed on the surface of the fabric. The reason for the hydrophobicity of the surface of the polycotton fabric is the decrease of surface tension. The previous study has found that waterborne polyurethane (WPU) coating decreased the surface tension of cotton fabrics to 72.8 dynes/cm, resulting in a water contact angle of 94° (Moiz et al., 2016). TPU coating is more effective in reducing the surface tension than WPU, and it decreases the surface tension to 46.2–39.4 dynes/cm for polycotton fabrics to be resistant to water and liquids/chemicals. The 8% PT coated polycotton fabric displays a water contact angle of 155 ± 4° with hysteresis of 0.36 ± 1°, and this is due to the further lower surface tension (22.0 dynes/cm) of PT (Wu et al., 2014, Zeng et al., 2015). The polydimethylsiloxane group in PT reduces the surface tension of polycotton fabrics. It is also noticed that the hydrophobicity is probably due to the rough surface of the coated fabric due to the particles on fibres. The water contact angles of TPTs are 139 ± 1° (hysteresis 1.49 ± 1°), 142 ± 7° (hysteresis 0.38 ± 1°), 140 ± 8° (hysteresis 8.01 ± 1°), and 127 ± 10° (hysteresis 9.39 ± 2°) with PT concentrations of 2, 4, 6 and 8%, respectively. The water contact angles of TPTs are slightly higher than that of TPU as shown in Figure 5-4, suggesting that PT further enhances the hydrophobicity of the TPU on the surface of polycotton fabrics. It is noted that the concentration of PT has little effects on the water contact angle. Compared with the water contact angle of WPU as reported (Moiz et al., 2016) , the TPT coating has resulted in an enhanced hydrophobicity evidently as the water contact angle (around 140°) is higher than that of WPT coating (around 127°). For comparison, the water contact angle of the widely-applied Gore-Tex is around 110°C, while TPT coating brings better hydrophobicity to fabrics with a higher water contact angle.

Durability of coating is always an issue as the linking between the coated components and the substrate is very weak, so it is very hard to maintain the added functions when the coated fabrics are subject to different cycles of laundering or crocking (Deng et al., 2010, Lin et al., 2015, Huang et al., 2011). The TPU-PDMS-TMS coating shows an excellent durability against laundering and crocking, as indicated in Figure 5-4. The PT coating shows a reduction of around 14% after laundering and crocking, and this is due to the removal of polydimethylsiloxane particles from the surface of the coated polycotton fabric. Statistical analysis suggests that the water contact angles after laundering and crocking are significantly different to the coated for 8% PT. However, TPU forms a smooth membrane on the surface of fibres and thus the durability against washing and crocking is very high, as shown in Figure 5-4.

The existence of TPU enhances the durability of PT, so that the TPT coatings with different concentrations of PT show reductions in water contact angle of less than 5% after laundering and crocking. PDMS alkyl chains have strong bonding strength between the fabric and the TPT coating, thus the durability of the coating is very high. The statistical analysis shows that the water contact angles are not significantly different for TPU and TPTs, indicating that the hydrophobicity is very durable against laundering and crocking.

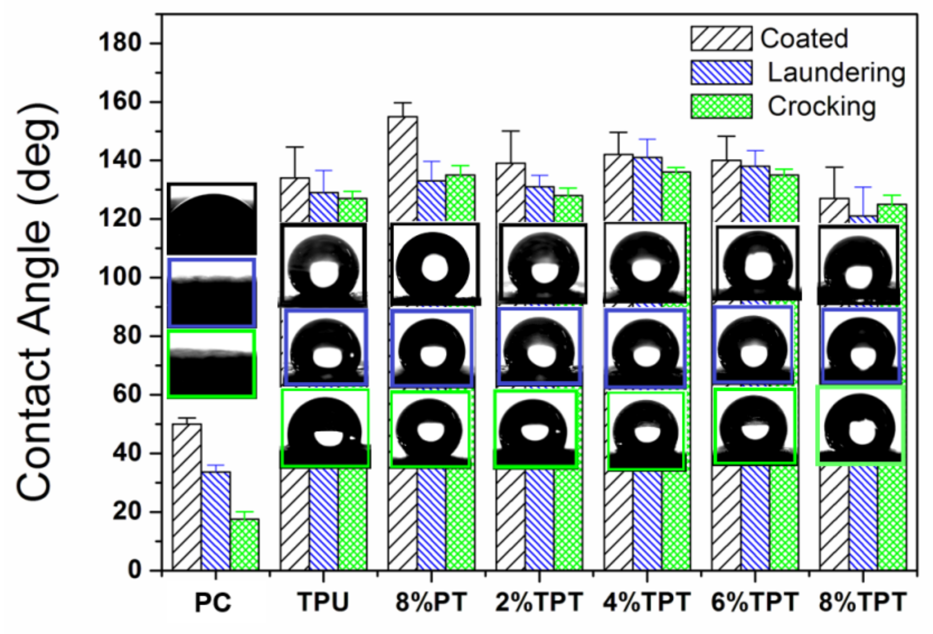

Figure 5-4: The water contact angles of the uncoated polycotton fabric, TPU coated, 8% PT coated and TPT coated with different concentrations of trimethylated silica (PT) (The photos in blue and green boxes refer to the water contact angle profiles after laundering and crocking, respectively).

It is noticed that for WPT coating there is an 8–15% reduction in water contact angle after laundering or crocking the coated fabrics (Moiz et al., 2016), the durability of TPT coating is thus more durable than that of WPT**.**

5.3.2.2 Water repellency

Polycotton fabrics are not waterproof, and the water repellency of the untreated polycotton fabric is as low as 50%. The low water repellency is due to the porous structure of the fabric and the wettability of the cotton fibres in the fabric. Coating of TPU has enhanced the water repellency to 70%, as shown in Figure 5-5. The surface of polycotton fibres has been covered with TPU membrane after coating (Figure 5-3(b)), so that water can only penetrate through the pores and channels of the fibrous structure. It is noted that PT coating brings 100% water repellency to polycotton fabrics. The surface energy of the PT coated polycotton fabric is very low due to the siloxane groups, resulting in a high-water contact angle and the absolute water repellency. TPT coated fabrics show the water repellency of 80%, suggesting a 10% enhancement than the TPU coated. However, the water repellency of TPTs is lower than that of 8% PT, and this is due to their relatively lower surface tension. The recrystallization of the alkyl long chains of PDMS leads to stronger bonding strength between the middle chains of TPU, thereby the water repellency of coated fabric has been enhanced (Roe and Zhang, 2009, Moiz et al., 2016).

The concentration of PT does not affect the water repellency of the TPT coated fabrics, as shown in Figure 5-5. It is evident that coating with TPU-PDMS-TMS has brought excellent water repellency to polycotton fabrics.

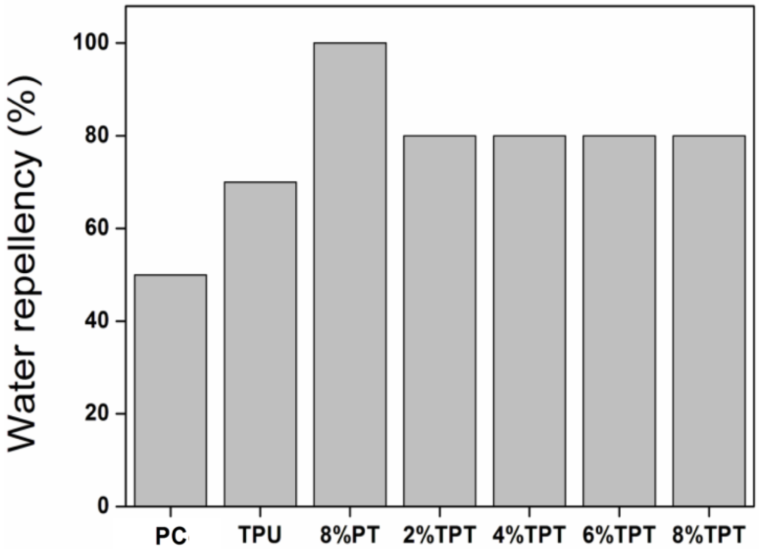

Figure 5-5: Water repellency of the uncoated polycotton fabric and polycotton fabrics coated with TPU, 8% PT and TPT with different concentrations of PT.

5.3.2.3 Oil repellency

The coated polycotton fabrics display different oil repellency, as illustrated in Figure 5-6. The TPU coated fabric shows good repellency to n-heptane, paraffin oil, and n-hexadecane, and this is because that the TPU coating has resulted in a high surface tension to prevent these hydrocarbons oils from penetrating into the coated fabric (Wang et al., 2011, Rengasamy and Mannari, 2013). The surface tension of TPU coated polycotton fabric is similar to n-decane (23.8 dynes/cm) and n-heptane (19.8 dynes/cm), so that the fabric is less repellent to them. The 8% PT coated polycotton fabric exhibits the poor repellency to n-heptane because the n-heptane has been used as the diluted solvent to prepare PT solutions.

The surface tension of 8% PT (22.0 dynes/cm) is very close to that of n-heptane (19.8 dynes/cm) and n-decane (23.8 dynes/cm), so that these oils penetrate into the fabric as shown in Figure 5-6. The droplet of n-hexadecane stays on the surface of the fabrics due to its relatively higher surface tension (27.3 dynes/cm) (Moiz et al., 2016).

From Figure 5-6 it is noticed that the 2% TPT shows excellent oil repellency against the castor oil, paraffin oil, vegetable oil and n-hexadecane. These droplets expand on the top layer of PT without penetrating into the underneath TPU layer. The oil repellency declines with the increase of the concentration of PT, and this is due to the resulted in lower surface tensions of the top layer that allow the droplets to penetrate into the fabrics. When the coated fabrics are under a tension, the repellency to some oils deteriorates, but in most cases, it remains the same. As shown in Figure 5-6, the repellency against castor oil drops gradually with the increase of tension for 4 % TPT and 6% TPT. Besides, the repellency against paraffin oil for 6% TPT drops evidently with the increase of tension. The oil repellency remains the same after laundering with only slight declines, but PT coating shows very poor durability against laundering. On the other hand, the oil repellency deteriorates apparently after crocking.

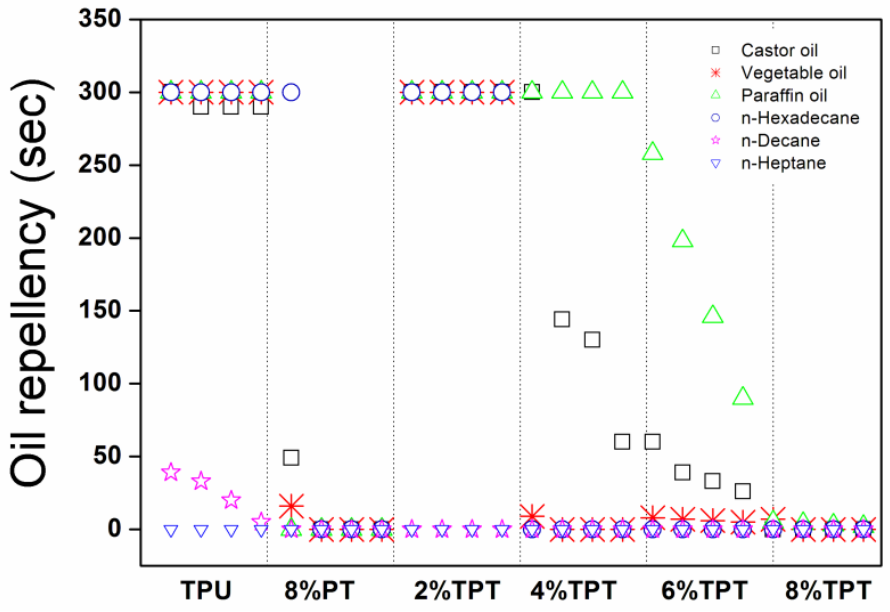

Figure 5-6: Oil repellency grades of fabric coated of TPU with different concentrations of PT. (For each sample, the four series of data from left to right stands for the oil repellency without tension and with the tension of 1, 3 and 5 NP, respectively).

5.3.2.4 Aqueous liquid repellency

Uncoated polycotton fabric is not resistant to aqueous liquids due to its hydrophilic property. The TPU coated control fabric to shows the excellent resistant to all kinds of water/alcohol aqueous liquids, as shown in Figure 5-7. It is also noted that the droplets on the TPU coated fabric are in the shape of semi-sphere. The 8% PT coated cotton fabric is repellent to all kinds of aqueous liquids except for the 60/40 one. The surface tension of the mixture of water/alcohol decreases from 44 to 24 dynes/cm with the increase of alcohol in the mixture. The surface tension of 8% PT is 22.0 dynes/cm, similar to that of the 60/40 one, thus the fabric is not resistant to the 60/40

(Moiz et al., 2016). Besides, the droplets on 8% PT are in the shape of the sphere, suggesting a better repellency than that of TPU coated. The reason for the better repellency from 8% PT is probably due to the higher superhydrophobicity as discussed earlier. The 8%TPT shows excellent repellency to all kinds of aqueous liquids, and the repellency is not altered after 300 seconds and when the fabric is subject to an external tension, as shown in Figure 5-7.

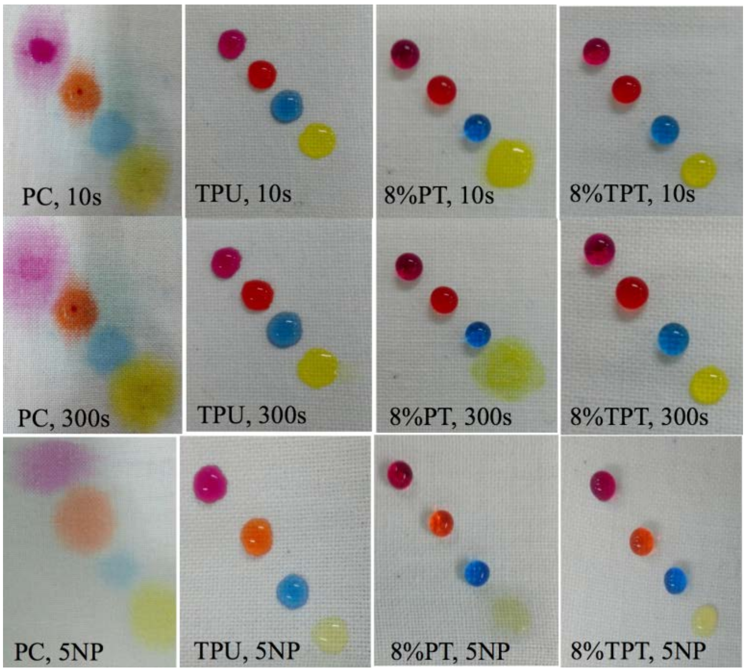

Figure 5-7: Aqueous liquid repellency of the uncoated polycotton fabric, TPU coated, 8% PT coated and 8% TPT coated fabrics (water/alcohol composition ratios are 98/2 for shopping pink, 90/10 for orange, 80/20 for blue and 60/40 for yellow, respectively).

5.3.2.5 Chemical resistances

Chemical resistance depends on the surface tension of the coated fabrics, and usually, the fabric is resistant to chemicals with higher surface tensions. On the other hand, if the surface tension of a chemical is closer to the coated fabric; the chemical will penetrate into the fabric within a short period of time. Polycotton fabrics are not resistant to chemicals due to their excellent wettability, as shown in Table 5-2.

The TPU-coated fabric shows excellent resistance to liquid chemicals, such as acetonitrile, acetic acid, butadiene, dimethylformamide, n-heptane, n-hexadecane, isopropyl alcohol, paraffin oil and sodium hydroxide. This is due to the higher surface tensions of these chemicals than that of the TPU-coated fabric. TPU coating brings omniphobic surface to the coated fabric with the excellent chemical resistance (Pan et al., 2012, Zeng et al., 2015). However, TPU coating is not resistant to n-hexane, triethylamine, and n-decane due to their similar surface tensions.

With its lower surface tension, the 8% PT coated fabric is limitedly resistant to chemicals including acetic acids, butadiene, dimethylformamide, n-hexadecane and sodium hydroxide. The TPT coating is resistant to most of the chemicals as indicated in Table 5-2, as the coating combines the resistance from both TPU and PT. An increase of the concentration of PT has limited effects on the chemical resistance. Similar to the oil repellency, the chemical resistance is not severely affected after laundering but it deteriorates evidently after crocking. It is evident that the TPT coating has brought the excellent chemical resistance to polycotton fabrics, and the versatile protective capacity of the coated polycotton fabrics can be applied in various areas where chemicals are involved.

Table 5-2: Chemical resistances (seconds) for all coated and uncoated cotton fabric.

Chemical	Surface tension (dynes/cm)	Poly cotton	TPU	8% PT	2% TPT	4% TPT	6% PT	8% TPT
n-Hexane	18.4	0	0	0	0	0	0	0
Triethylamine	19.7	0	0	0	0	0	0	0
n-Heptane	19.8	0	300	0	300	300	300	300
Methanol	22.1	0	146	0	69	75	85	137
Isopropyl alcohol	23.0	10	300	10	300	300	300	300
Acetone	23.2	0	70	10	5	16	30	57
n-Decane	23.8	0	40	0	13	6	5	4
Paraffin oil	26.0	0	300	16	300	45	50	57
Tetrahydrofuran	26.4	0	62	0	82	91	141	167
Dichloromethane	26.8	0	70	5	0	16	30	35
n-Hexadecane	27.3	0	300	300	118	30	29	28
Acetic acid	27.0	0	300	300	300	300	300	300
Toluene	28.4	0	185	0	0	0	0	0
Acetonitrile	28.7	0	186	0	114	228	289	297
Dimethylformamide	36.7	0	300	300	300	300	300	300
Butadiene	47.0	0	300	300	300	31	16	10
Sulphuric acid	84.0	0	300	300	300	300	300	300
Sodium hydroxide	101.0	0	300	300	300	300	300	300

5.3.3 Comfort

5.3.3.1 Air permeability

Air permeability of the untreated polycotton fabric is 95 cm/s, indicating that the airflow can easily penetrate through the pores of the fabric. Coating inevitably blocks the pores of fabrics and thus the air permeability of the as-coated fabrics usually deteriorates (Lomax, 2007, Jassal et al., 2004, Kang et al., 2007). As shown in Figure 5-8, the TPU-coated fabric has an air permeability of 3.3 cm/s and the 8% PT has that of 4.76 cm/s. It is evident that TPU coating has evident effects in blocking the pores of polycotton fabrics than PT. TPT coated fabrics have even lower permeability than that of TPU, and the permeability decreases further with the increase of the concentration of PT. The adding of PT on the top of TPU would further block the pores between the neighbouring fibres, thus the air permeability decreases further with the increase of the concentration of PT. Nevertheless, the air permeability has been improved by replacing WPU with TPU in the coating (Moiz et al., 2016). WPT coating shows an air permeability of 0.1-0.2 cm/s, which is much lower than that of TPT coating. WPU forms a uniform membrane on the surface of cotton fabrics without fibres being seen from SEM photos, while TPU coating does not fully cover the surface of the fabric with fibres observable from SEM photos. TPT coating thus allows air to penetrate through the limitedly preserved pores of the fabrics, resulting in higher air permeability than WPT coating.

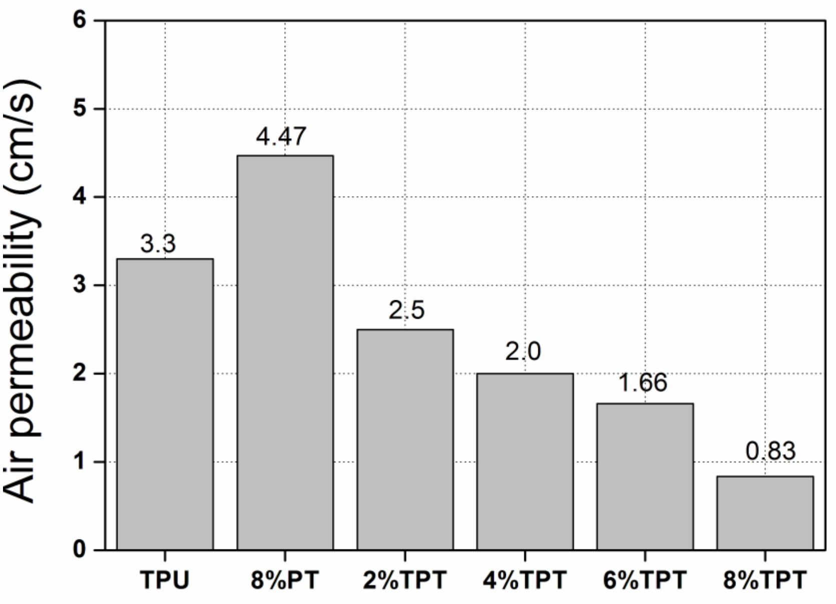

Figure 5-8: Air permeability of polycotton fabrics coated with TPU, 8% PT, and TPTs with different concentrations of PT.

5.3.3.2 Water vapour resistance and permeability

Water vapour resistance is the factor to determine the breathability of fabrics. TPU coating has deteriorated the water vapour permeability of polycotton fabrics; the water vapour resistance and permeability index are shown in Figure 5-9. This is due to the blocking of the pores of polycotton fabrics by the TPU membrane. The coating of PT doesn't affect the breathability of polycotton fabrics much as most of the pores within fabrics are preserved.

The increase of the concentration of PT in TPT coatings has significant effects on the breathability of the coated fabrics, and the higher the concentration of PT, the higher the water vapour resistance (Havenith, Heus & Lotens 1990). In this case, the increase of the thickness of the coated layers from increasing the PT concentration results in the worse breathability as more pores of the coated fabrics have been blocked. For comparison, Gore-Tex has an excellent breathability, the TPT coating doesn't exhibit as good breathability as Gore-Tex though its surface is more superomniphobic.

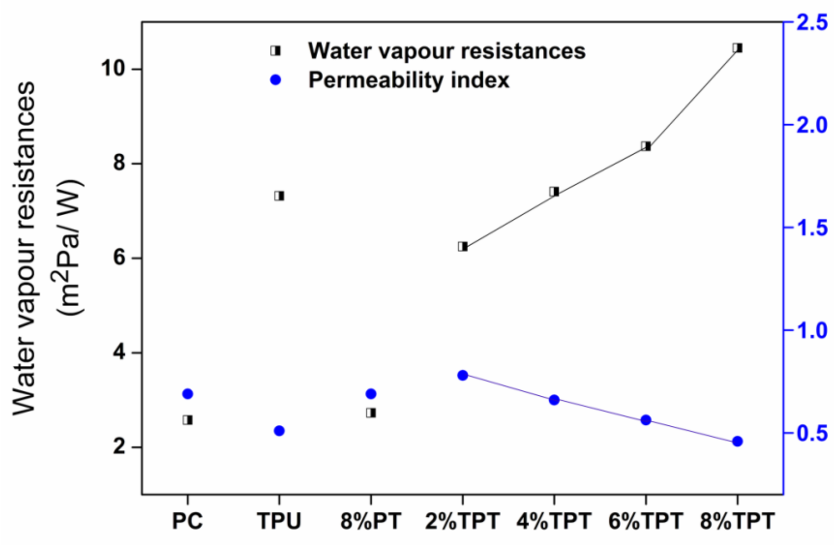

Figure 5-9: Water vapour resistances and permeability index of the uncoated fabric polycotton fabric, 8% PT coated and TPT coated with different concentration of PT.

5.3.3.3 Thermal resistance

The thermal resistance of polycotton fabrics is enhanced after coating, as shown in Figure 5-10. The uncoated polycotton fabrics have open pores (as shown the inset) to allow heat exchange between the hotplate and the environment so, that the thermal resistance is very low. The PT coated polycotton fabric has a similar fibrous structure as indicated in the inserted SEM photo, but the thickness of the coated fabric is higher than the uncoated. The thermal resistance of PT coated polycotton fabric is thus slightly higher than that of uncoated (Majumdar et al., 2010), but the data of thermal resistance is not significantly different according to the standard deviations in Figure 5-10. TPU coating exhibits a thermal resistance of 0.085 m^2K/W, which is much higher than that of the uncoated polycotton fabric (0.063 m^2K/W) with a statistically significant difference. The enhancement of thermal resistance after coating of TPU is due to the blocking of the open pores, as shown in the inserted SEM photo. The blocked pores capture static air within the fibrous structure, resulting in less heat transfer with a higher thermal resistance. The thermal resistance of TPTs is similar to that of TPU, with a significant difference in the untreated cotton fabrics. The increase of PT concentration in TPT coating has limited effects on the thermal resistance, as seen in Figure 5-10. In this case, the enhancement of thermal resistance is mainly from the blocking of open pores within the fibrous structure, whereas the increase of thickness of the coating does not contribute much to the increase of thermal resistance.

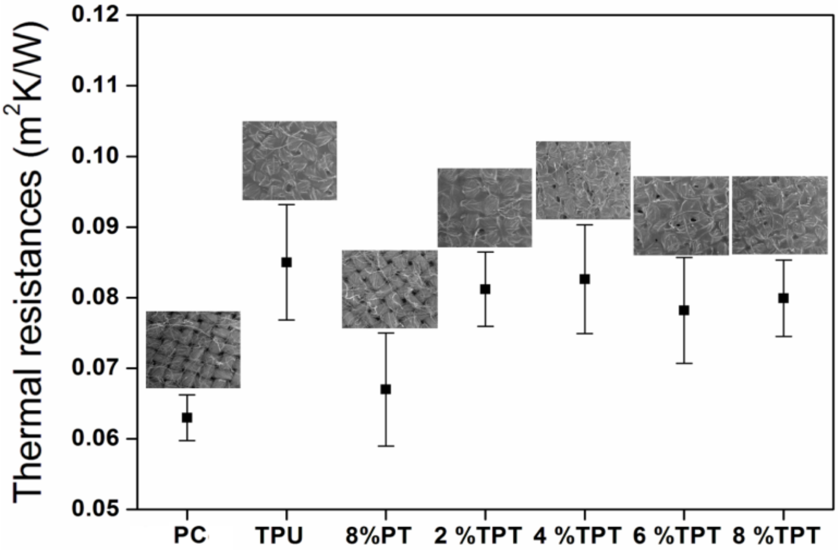

Figure 5-10: Thermal resistances of cotton fabric, TPU coated and TPT coated with different concentrations of PT.

5.3.3.4 Moisture management properties

The moisture management property of polycotton fabrics has changed after the coating, as indicated by the MMT profiles in Figure 5-11. For polycotton fabrics, water can transport across the fibrous structure easily due to its excellent wettability and wicking property (Kar et al., 2007, Shaid et al., 2014). There are no evident differences between the top and bottom surfaces for polycotton fabrics in terms of the MMT index, as shown in Table 5-3. Coating of TPU has made the top surface of the polycotton fabric smooth for water to spread, as shown the MMT profile with a larger wet area. However, a smaller amount of water has been transported to the bottom surface so, that the one-way transport capability is significantly lower. It is evident that TPU coating has enhanced the water spreading performance on the top surface but deteriorated the water transport capability of the polycotton fabrics. The overall moisture management capacity (OMMC) has changed from 0.47 to 0.04 after TPU coating.

The water droplet on 8% PT appears as a sphere, as shown in Figure 5-11. The rough surface and low surface energy of PT have made the polycotton fabric surface superhydrophobic, thus the water does not spread on the top surface or does not it transport to the bottom side. The bottom surface has not been wetted, as shown the profile in Figure 5-11.

Table 5-3: Moisture management properties of cotton fabric, TPU coated and TPT coated with different concentrations of PT (measure time = 120.00 seconds).

MMT index	**Polycotton**		**TPU**		**8%PT**		**2-8%PT**	
	Top surface	Bottom surface	Top surface	Bottom surface	Top surface	Bottom surface	Top surface	Bottom surface
Wetting time (s)	5.9	5.99	4.68	12.23	8.42	120	7.58–9.54	120
Absorption rate (s)	5.73	15.93	67.98	4.89	253.66	0	90.20–406.33	0
Maximum wetted radius (mm)	15	15	25	0	5	0	5	0
Spreading speed (mm/s)	2.47	3.2	4.84	0	0.58	0	0.51–0.64	0
One way transport capability	62.08		–624.90		–995.77		−988.00- −1086.26	
OMMC	0.47		0.04		0		0	

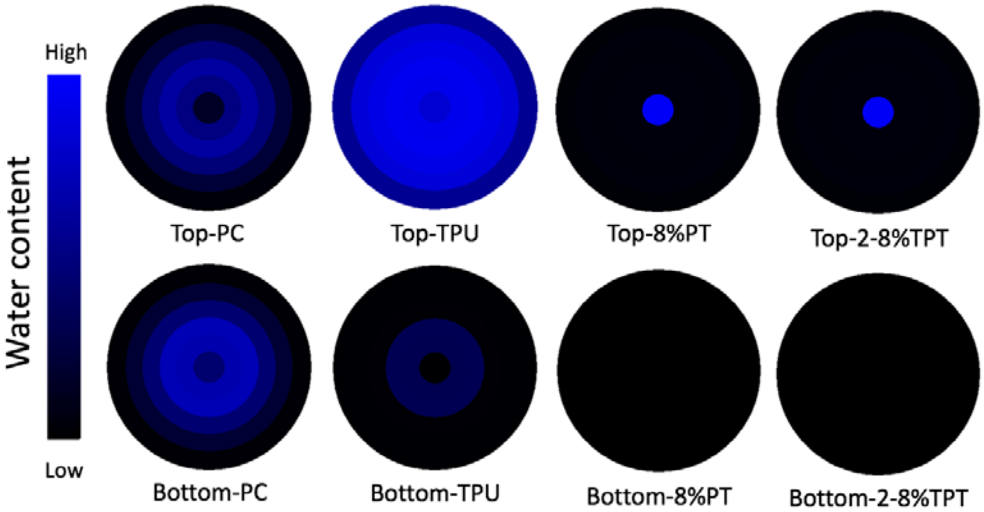

Figure 5-11: Moisture management tester (MMT) profile of the uncoated polycotton fabric, TPU coated 8% PT coated and TPT coated with different concentrations of PT.

It is evident that PT coating has made the polycotton fabrics superhydrophobic and water cannot penetrate through the fabrics. Besides, TPT coatings have the similar moisture management property with PT coating, and this is due to the existence of PT on the surface from these coatings.

5.4 Summary

A soft, flexible, highly durable, comfortable and versatile protective coating for polycotton fabrics was developed by the pad-knife-pad coating of TPU-PDMS-TMS. The coating brought a thin layer to the surface of fibres while the fibrous structure of the fabric was not severely affected. The active TPU combined with PDMS-TMS to form a cross-linked network, providing flexible and soft segments with low surface energy siloxane groups to the polycotton fabrics. The coated polycotton fabrics showed a superhydrophobic surface with a water contact angle of 142–155° and the superhydrophobicity was durable against different cycles of laundering and crocking. The enhanced durability of the samples has been achieved through the recrystallization of the long chains of the methyl groups of the PDMS and Si–OCH_3 bonding imparted between the substrate and the TPT coating. The coating also showed the excellent repellency against water, oil, aqueous liquids and different chemicals. The versatile protection was not noticeably affected when the fabric was subject to tensions. The air permeability together with the water vapour permeability of the polycotton fabrics deteriorated after coating due to the blocking of pores by the deposited TPT. The thermal resistance of the coated polycotton fabrics was higher than that of the uncoated polycotton fabric due to the trapping of static air within the fabric structure by the coated layers. TPU coating enhanced the water spreading capacity on the surface of polycotton fabric but deteriorated the water transport capacity. The TPT coated fabrics exhibited water droplets on their surface and showed poor moisture management capacity.

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6 DURABLE SUPEROMNIPHOBIC SURFACE ON COTTON FABRICS VIA COATING OF SILICONE RUBBER AND FLUORO-POLYMERS

6.1 Introduction

Clothing is mainly used for aesthetic favour and protection. In some extreme cases, clothing has to provide higher level protection for the wearer to withstand hazards and threats from the environment (cold, hot, wind, water, soil, gas, etc.) or other sources (fire, explosion, corrosive chemicals, and pollution). Performance textiles have been developed to prevent human for these purposes (Owen and Dvornic, 2012, Lin et al., 2015). As a very important performance textile, protective clothing has seen a big success in the past years. With different products developed, protection clothing with solo function, such as flame retardant (Xiang et al., 2017, Holme, 2007), water repellency/superhydrophobicity (Chen et al., 2018), oil repellency (Wang et al., 2011), self-cleaning (Zeng et al., 2015), cold protection (Emelyanenko et al., 2017), chemical protection (Zeng et al., 2015) and moisture management has been widely developed to serve customers in different areas (Shin, 2005, Xiang et al., 2017). Recent research and development are focusing on multiple protection of performance textiles (Lu et al., 2017), because protective clothing is usually used in complex situations in which wearers must be protected from different threats from environment and incidents. Against this background, the omniphobic surface of textiles has been the research focus (Pan et al., 2012), and the developed products have the capability of protecting skin from hazardous liquid chemicals, industrial chemicals, petroleum oils, and lubricants.

Development of new fibres and functionalization of current fibres is the key to advance technology towards the next generation performance textiles. High-performance fibres are developed with their intrinsic properties to fulfil the heat and fire protection needs, such as protective clothing, commercial fabrics use in liners, curtain and transport materials, medical and military garments (Horrocks, 2014), Kevlar for ballistic resistance (Park et al., 2014), carbon fibre (Thakare et al., 2017), nanofibres (Fang et al., 2012). However, most protection would need a special fabric surface in which surface and interface functions are crucial. Much attention has been put on functionalization of fabric surface for the development of performance textiles, and different technologies have been developed including Plasma-enhanced chemical vapour deposition (PCVD) (Tan et al., 2012), plasma (DeCoste and Peterson, 2013), grafting (Satam et al., 2010), coating (Singh and Singh, 2017).

A coating is regarded as the most feasible and applicable technology for developing performance surface on fabrics. The coated materials and the chemical reaction together with the developed surface structure are the determining factors of the targeted performance. Easy conducting and feasibility of industrial application are the key to develop coating technology and robust coating technology including knife coating (Moiz et al., 2016), dip coating (Lin et al., 2015), Electrospinning coating (Kang et al., 2007), and combined coating (Schutzius et al., 2011) have developed. From the materials side, the coated layer usually exhibits a low surface tension to withstand different substances. Polyurethane, silicone rubber, and fluoro-compounds are the most widely used materials in the functional coating of textiles (Nouri and Saadat-Bakhsh, 2017, Seitz et al., 2016). The development of Gore-Tex® has seen a big success in which the polytetrafluoroethylene (PTFE) film is used to functionalize textiles (Kang et al., 1996). However, some fluorine-based substances, such as perfluoro-octane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) of carbon chains greater than six are restricted in the functional coating of textiles due to the health issues these compounds cause to human. Searching for replacement of fluoro-polymers is on the way of developing protective clothing (Hekster et al., 2002).

The development of superomniphobic surface would require the developed coating layer to withstand a series of agents, thus the combination of materials and the combined action of different coating methods are required in the process. The previous endeavour has found the combination of polyurethane with polydimethylsiloxane and trimethylated silica exhibits versatile protection on cotton fabrics (Moiz et al., 2016) and polycotton fabrics (Moiz et al., 2017). Actually, there are many fluoro-polymers that are environmental friendly, such as oleophobol, phobol and Trimethylmethoxysilane (TMMS) (Dhiman and Chakraborty, 2014). This work would focus on the combined coating of rubber membrane and environmental friendly fluoro-polymers to achieve superomniphobic surface on cotton fabrics. The coated fabrics were characterized by chemical analysis, handle, morphology and protection against different agents including water, oil, an aqueous liquid, chemicals and soil, and the comfort of the coated fabrics were studied to better understand the effect of coating on clothing. The developed coating technology would benefit the development of the next generation performance textiles for versatile protection.

6.2 Experimental

6.2.1 Materials

Cotton fabrics were purchased from Bruck Textiles, Australia. Isys HPx was purchase from CHT Pty Ltd, Germany. Rubber membrane (SILASTIC 1951-200P, LSR), in paste form, was purchased from Dow Corning Europe S.A, Belgium. Invadine PBN, Kinttex ® FEL, Phobotex RSH, Phobol ® CP-C and Olephobol® CP-C were purchased Huntsman Singapore Pty Ltd. Trimethylmethoxysilane (TMMS), n-Hexadecane and n-Decane were purchased from Sigma Aldrich Pty Ltd, Australia. Mineral oil was purchased from Johnson and Johnson Pacific Pty Ltd, Australia. Acetonitrile, isopropyl alcohol and dichloromethane (Ana-R) were purchased from BDH Limited Poole, England. Sulphuric Acids (98%) was purchased from RSL LAB SCAN Ltd, Thailand. Dimethylformamide was purchased for Merck, Germany. Sodium Hydroxide was purchased from Chem Supply Pty Ltd, Australia.

6.2.2 Methods

A conventional dipping-padding-knife-curing method (Moiz et al., 2016, Moiz et al., 2017) was applied to perform the coating on cotton fabrics, as shown in Figure 6-1(a). The cotton fabric was wetted by 0.01% (w/v) Triton X-100 solution in water for 30 minutes and scoured by caustic soda at 90°C for 1 hour. Scoured fabrics were rinsed in warm water and then in cold water. Rinsed fabrics were left overnight for hanging dry in an ambient environment. To impart hydrophobic properties on fabrics, various chemical coatings were applied on the fabric using an Ernst Benz Pad machine. Fabrics were passed through the machine at a pad speed of 2 m/min at 8 kPa/cm pressure. While padding, 10% solution of the chemical was applied and each fabric sample was passed through the pad three times to ensure even layering of the chemical on the fabric surface. These samples were then dried at 60° C for 30 minutes and cured at 160° C for 5 minutes.

At first, cotton fabrics (A) were padded with a single layer of the chemical solutions on the fabric surface. As shown in Figure 6-1(b), a solution of 5 g/100 ml of Isy Hpx with 95 ml distilled water was applied to the fabric surface to test its reaction. The solution acted as a cation cross-linking agent to network the repellent chemical layers on the fabric. A single layer of rubber membrane was coated on the padded fabrics by knife-edge coating method. The coating consisted of (LSR (part a (90.0 g) + part b (10.0 g) and was applied uniformly on the fabrics (B). Using the same padding method, fluoro-polymers Phobol CP-C (10% Solution) and Oleophobol CP-C (10% solution) were applied on the fabric surface and a percentage pickup of the chemical after padding on the cotton fabric was calculated. The further padded fabrics were denoted as sample C and D, respectively. Alternatively, a double layer of TMMS + Phobol was padded onto the Isys Hpx padded fabric to make sample E.

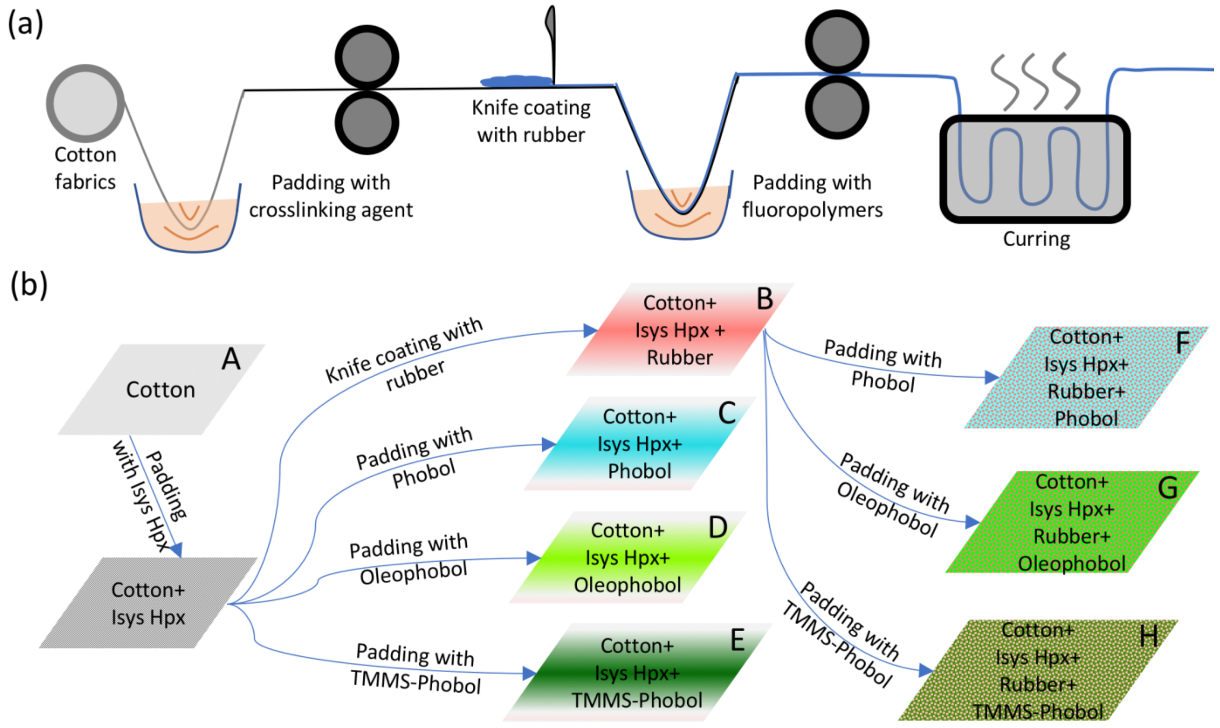

Figure 6-1: Schematics of the pad-knife-pad-cure method (a) and experimental design (b).

In order to study the combination of rubber membrane and fluoro-polymers, three different samples were prepared by applying the multi-layer coating on the surface of cotton fabrics (Figure 6-1(b)). It included triple layers of Isy Hpx + rubber membrane + Phobol (F), Isy Hpx + rubber membrane + Oleophobol (G) and Isy Hpx + Rubber membrane + TMMS + Phobol (H).

6.3 Results and discussion

The multi-layer coating has resulted in a cross-linked network on the surface of cotton fabrics, as illustrated in Figure 6-2(a) the mechanism of the coating. With Isy Hpx acting as the cross-linking agent in the first padding process, a cross-linked network between the rubber membrane and the fluoro-polymers has been formed. Strong bonding between the CH_3 groups of rubber and the CF_2 groups of fluoro-polymers has been established after the curing process, bringing durability of the coated layers. As a result, the surface appearance, morphology, handle, thickness and chemical components of the surface of cotton fabrics have been changed. Meanwhile, the protection of the surface has been enhanced with comfort compromised to a certain level.

6.3.1 Characterization

6.3.1.1 Morphology of fabrics

Figure 6-2(b) shows the optical photos of all the samples. It is evident that rubber coating has resulted in a membrane with shiny appearance on the surface of fabrics, as shown the optical photos of samples B, F, G and H. Whereas, the padding of fluoro-polymers (samples C, D, and E) have not affected the fibrous structure much as compared to uncoated cotton fabrics (sample A).

SEM photos have further confirmed the surface morphology of all the samples, as shown in Figure 6-2(b). The typical morphology of cotton fibres is shown in the photo for sample A, indicating the convolutional ribbon profile of cotton. The samples padded with fluoro-polymers (samples C, D and E) show clear fibrous structures, but the structure of these samples is more compact than that of sample A. The squeezing involved in the padding process has forced the fibres together with fluoro-polymers impregnated into the fibrous structures, resulting in the compacted structure of the padded samples. On the other hand, samples B, F, G, and H show a membrane on their surface with some fibres and particles, and the fibrous structure has been severely altered by the coating of rubber. A quite uniform membrane has been formed on the surface of fabrics after coating with rubber, and it is evident that this layer will act as the barrier to withstand water, oil, and chemical from penetrating onto the fabrics. Unfortunately, the membrane blocks the pores of the fibrous structure, and thus the comfort of the as-coated fabrics will be deteriorated accordingly.

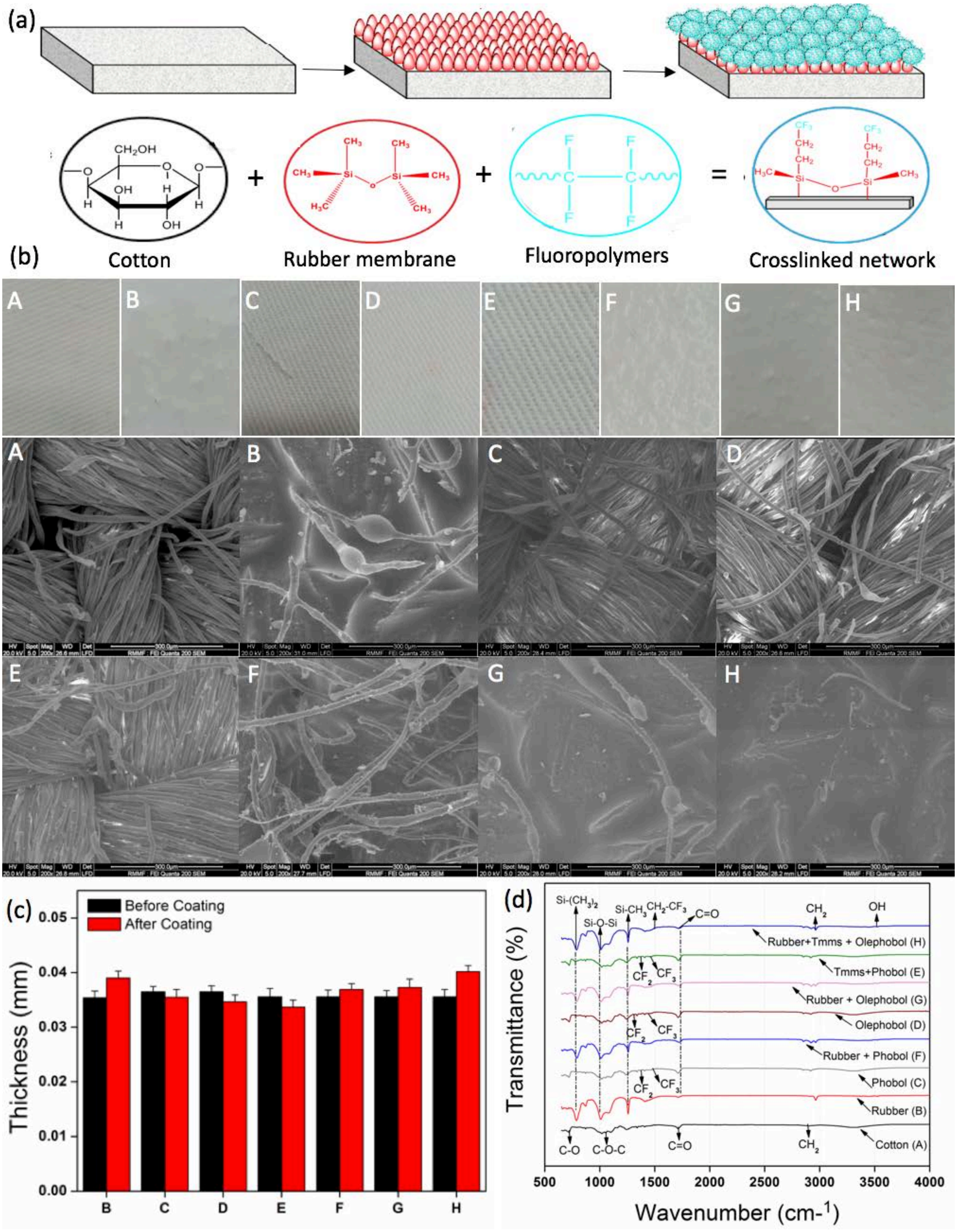

Figure 6-2: (a): Schematics of the mechanism; (b): Optical photos and SEM photos; (c): Thickness; (d): FTIR spectra.

6.3.1.2 Thickness

The thickness of coated fabrics is different from the uncoated fabrics depending on the coating methods and the as-coated materials. Figure 6-2(c) illustrates the thickness of cotton fabrics before and after different scenarios of coating Figure 6-2(b).

The thickness of fabrics after padding usually decreases due to the squishing of the rollers, resulting in thinner fabrics with a more compact fibrous structure. As shown the thickness of samples C, D and E in Figure 6-2(c), fabrics after padding ended up with a lower thickness no matter what fluoro-polymers or silicone were used.

Knife coating usually results in a uniform membrane on fabric surface with a larger thickness. Cotton fabrics coated with rubber (sample B) show an evidence increase in thickness as indicated in Figure 6-2(b). Further padding of fluoro-polymers on the coated rubber surface would reduce the thickness a little bit due to the squeezing effect, so that the thickness of sample F and G is relatively lower than that of sample B. However, sample H shows the highest thickness due to the multi-layer of fluoro-polymers that were added to the rubber surface.

6.3.1.3 Handle

The cotton fabrics exhibit different handle after the padding and coating processes. The stiffness of fabrics is different before and after coating. Cotton fabrics are flexible with a bending length of 2.2 cm and flexural rigidity 0.12 mg/cm, and this is due to the loose woven structure as shown in Figure 6-2(b). Padding has ended up with a compact fabric structure for cotton fabrics as suggested by the SEM photos, thus the padded fabrics become inflexible, hard and stiffer (Yüksekkaya, 2008, Ye et al., 2006). As a result, the bending length and flexural rigidity for fluoro-polymers padded cotton fabrics (samples C, D and E) are around 2.3 cm and 0.17 mg/cm, respectively. It is noted that padding of fluoro-polymers has not affected the stiffness much, considering the slightly changed stiffness. However, a coating of rubber has the dramatic effect on the stiffness of cotton fabrics. The formation of rubber membrane within and on the surface of the fibrous structure has made the fabrics rigid and stiff. The bending length and flexural rigidity of rubber coated samples (B, F, G, and H) have been enhanced to 3.4-3.9 cm and 1.35-2.22 mg/cm. Especially, the coating of rubber plus Phobol (sample F) showed the highest stiffness.

The surface friction and roughness of cotton fabrics are also different after the coatings. The coefficient of surface friction (MIU) and geometrical roughness (SMD) of cotton fabrics (A) and fluoro-polymer coated fabrics such as C, D, and E are almost the same with the value change around 0.16-0.18 μm and 4.0-4.2 μm for MIU and SMD, respectively. It is evident that fluoro-polymers coating has no obvious effect on the surface friction and roughness of cotton fabrics even though particles of fluoro-polymers have been formed on the surface of fabrics. However, with rubber membrane coated (samples B, F, G, and H), the surface friction together with geometrical roughness have been increased to 0.2-0.3 µm and 5.6-6.4 µm, respectively (Baek and Khonsari, 2008).

6.3.1.4 FTIR spectra

The FTIR spectra of all the samples are depicted in Figure 6-2(d). The cotton fabrics (sample A) represent peaks around 2962 cm^{-1}, attributing to the asymmetric and symmetric stretching of the C-H bond of the methyl group. The bands at 3400 cm^{-1} are assigned to the O-H stretching for vibration bonding. The rest bands at 1425, 1250 and 1072 cm^{-1} are due to the C-H bending, C-H and C-O-C stretching, respectively.

The cotton fabrics coated with the rubber membrane (sample B) show the peaks at 1258, 1080, 1009 and 792 cm^{-1}, cross-pounding to the Si-CH_3 and Si-O-Si groups of rubber. Individual spectra of phobol, oleophobol and TMMS as seen in Figure 6-2(d), (sample C, D, and E) present clear peaks of CF_2 and CF_3 groups at around 1338 and 1208 cm^{-1}, respectively. After the coating of rubber membrane combined with the fluoro-polymers (sample F, G and H), the peaks for the functional groups of fluoro-polymers (CF_2 and CF_3) have slightly shifted due to the formation of tri-fluoro-acetic anhydride (-Si-CH_2-CF_3) as a result of their polymerization reactions with cyclic organo-silanes (Tan et al., 2012). Fluoro-polymers have been involved to make the hydrophobic surface on cotton fabrics as shown in these FTIR spectra (Lin et al., 2015). The CF_2 and CF_3 were deformed and mixed with other rocking bands at 1338 to 1330 cm^{-1}. Other peaks in the range of 1100 to 650 cm^{-1} represent the bands of fluoro-polymers combined with rubber. Overall, surface functionalization of fluoro-polymers combined with rubber membrane has been evidenced by the FTIR spectra.

6.3.2 Protection

Due to the combined effect of fluoro-polymers and rubber membrane, a superomniphobic surface has been created on the surface of the coated cotton fabrics. The developed performance fabrics showed excellent protection against water, liquids, oils, different chemicals and soil.

6.3.2.1 Water contact angle

Figure 6-3(a) illustrates the WCA of all the coated cotton fabrics with the profiles of the water droplet on each fabric. Cotton fabrics are hydrophilic and a droplet of water can penetrate and sink into the fabrics within a second. The WCA of uncoated cotton fabrics is around 30-50°. The developed coating has apparently made the fabrics resistant to water, and the water droplets can stay on the surface of the as-coated fabrics (as shown the profiles of water droplets in Figure 6-3(a).

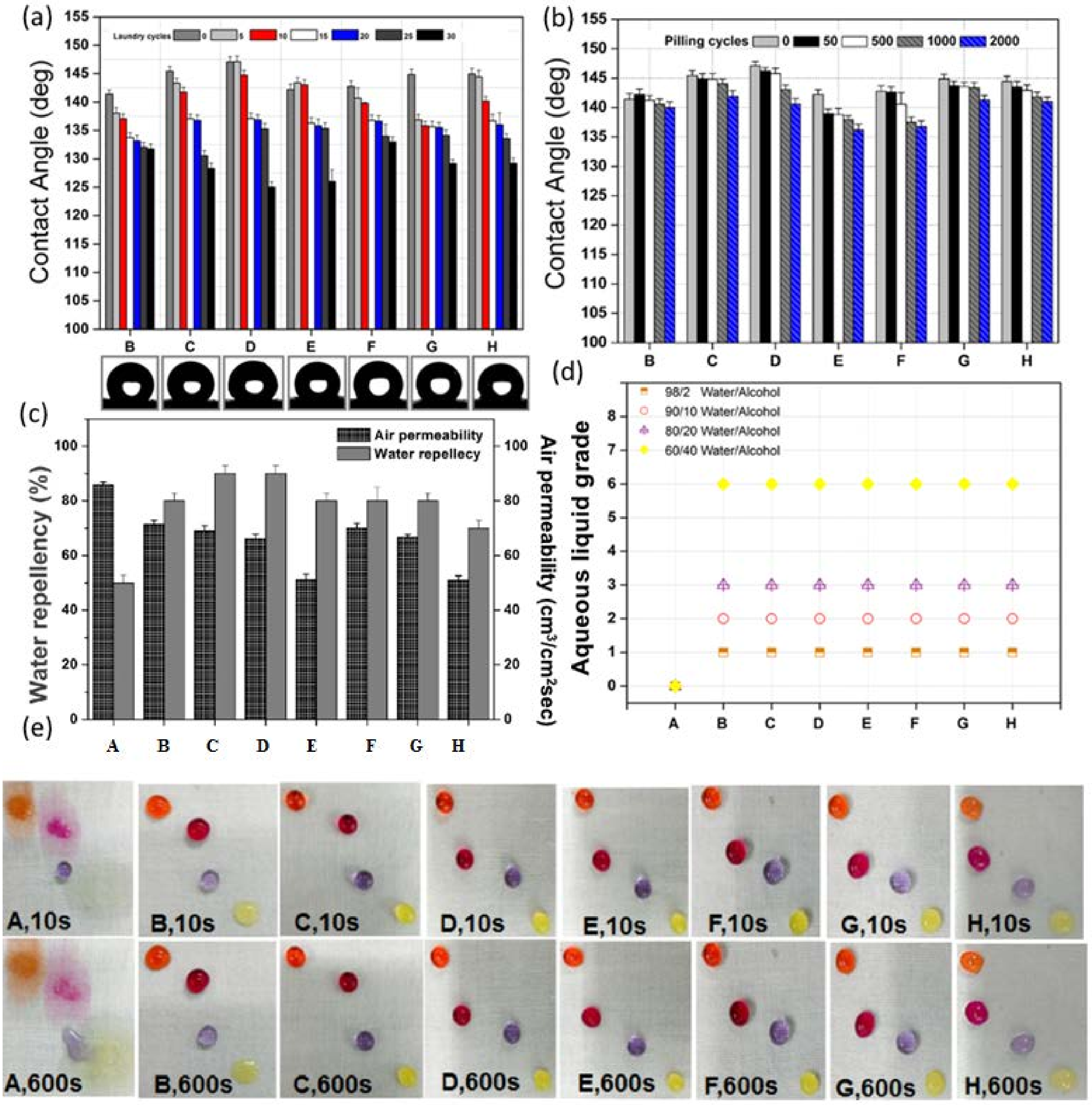

Figure 6-3: Protection of the as-coated cotton fabrics against water and aqueous liquids: (a) WCA after laundering (Photos: WCA profiles); (b) WCA after pilling; (c) Water repellency and air permeability; (d) Aqueous liquid repellency; (e) Photos of droplets of aqueous liquids on the surface of cotton fabrics (Water/alcohol ratios: Orange 98/2; Pink 90/10; Purple 80/20; Yellow 60/40).

Coating of rubber has brought a membrane with particles onto the surface of cotton fabrics, the surface roughness has been enhanced and the surface energy been reduced. The WCA for rubber coated fabrics is 141° as shown the sample B in Figure 6-3(a). Fluoro-polymers have very evident hydrophobic effect and the treated fabrics usually exhibit a WCA of around 150°. Phobol, oleophobol and TMMS-phobol were used to generate the surface roughness on cotton fibres, and the treated cotton fabrics show a WCA of 145° (C), 147° (D) and 142° (E), respectively. The combination of rubber membrane and fluoro-polymers (phobol, oleophobol and TMMS-phobol) has resulted in a WCA of 142° (F), 144° (G) and 145° (H) for the coated cotton fabrics. The enhancement of WCA to cotton fabrics is due to the low surface tension and the roughness of the coated rubber and fluoro-polymers.

The durability of the coating is the determining factor of the as-developed performance textiles because the products are subject to different cycles of washing and different mechanical movements. Figure 6-3(a) shows the WCA of all the coated samples after different cycles of laundering. The coating of rubber shows excellent durability as the reduction of WCA is 7.0% even after 30 cycles of laundering. The durability of rubber coating is probably due to the excellent membrane-forming properties of rubber which can withstand repeated washing. Fluoro-polymers coatings show poor durability (samples C-E in Figure 6-3(a)), and the reduction of WCA is 11.7%, 15.0%, and 12.0%, respectively. Fluoro-polymers coating results in particles on the surface of cotton fabrics that bring hydrophobicity to the coated fabrics. However, the bonding between cotton fibres and the fluoro-polymers is very poor. The poor durability of the fluoro-polymers is due to the removal of the formed particles on the surface of cotton fabrics after washing. The combination of rubber and fluoro-polymers (samples F-H) show enhanced durability, and the reduction of WCA is 7.0%, 9.7%, and 10.3%, respectively. Compared with the reduction of WCA of fluoro-polymers coating, the combination of rubber and fluoro-polymers has enhanced the reduction of WCA by 4.7%, 5.3% and 1.7% for phobol, oleophobol and TMMS-phobol, respectively. As discussed in the mechanism, a cross-linked network has been formed between rubber and fluoro-polymers after the establishment of the bonding between the CH_3 groups of rubber and the CF_2 groups of fluoro-polymers. The cross-linked network is rather strong to withstand washing; thus, the combination of rubber and fluoro-polymers shows enhanced durability.

Figure 6-3(b) shows the durability of the coated cotton fabrics after different cycles of pilling. All the samples show excellent durability against pilling, suggesting the strong adhesion between the coated layers and the cotton fabrics to withstand mechanical movements. Rubber membrane shows the best durability against pilling as the WCA doesn't change much even after 2000 cycles of pilling. An evident reduction of WCA can be seen for the coatings with fluoro-polymers while the combination of rubber and fluoro-polymers shows enhanced durability as expected. The cross-linked network between rubber and fluoro-polymers has better durability when the coated fabrics are subject to pilling, and this is due to strong bonding within the network.

6.3.2.2 Water repellency and air permeability

The hydrophobicity of cotton fibre and the porous fibrous structure make cotton fabrics a low water repellency of 50% cotton fabric (Moiz et al., 2016). The water repellency of the coated fabrics is much higher than that of cotton fabrics (Figure 6-3(c)) due to the surface hydrophobicity and the altered surface structure. Coating of rubber has resulted in a membrane on the surface of cotton fabrics, and thus the water repellency is as high as 80%.

The rubber membrane is not absolutely waterproof, suggesting some pores exist within the membrane to allow the penetration of the 20% of the water. The water repellency of coated surface with fluoro-polymers is 90% for sample C and D, and 80% for sample E. The lower surface tension of fluoro-polymers shows excellent resistance to water as compared to the rubber membrane. Besides, the forming of particles on the surface of fabrics blocks some the pores of the fabrics, so that the water repellency has been enhanced.

The combination of rubber and fluoro-polymers has not contributed to the enhancement of water repellency further, and the repellency is 80% and even 70% for sample H. As the fluoro-polymers have been coated on the rubber membrane rather than on the cotton fabrics, the pores from fibrous structures are just covered by the rubber membrane. The blocking effect from the formed particles is not as evident as sample C, D, and E, resulting in a relatively lower water repellency.

The air permeability of cotton fabrics has been affected by coating, as the results shown in Figure 6-3(d). The pore size and the fibrous structure usually determine the air permeability or the breathability of the fabrics (Jassal et al., 2004, Fang et al., 2012). Cotton fabrics show the air permeability of 86 cm/s. The coating of rubber membrane on cotton fabrics has resulted in the air permeability of 70 cm/s. The decline of air permeability is due to the blocking of pores by the rubber membrane. Coating of fluoro-polymers has created many particles to block the pores of cotton fabrics, thus the air permeability is similar to that of rubber coated one. However, sample E shows the air permeability of 50 cm/s as the TMMS-phobol has the maximum blocking effect to the pores within the fibrous structure. On the other hand, the air permeability of the combination of rubber and fluoro-polymers is similar to that of rubber or fluoro-polymer coated ones. Since the fluoro-polymers are coated on the surface of rubber membrane, the blocking effect from the formed particles is not evident as that on the surface of cotton fabrics.

6.3.2.3 Aqueous liquid repellency

Figure 6-3(d) shows the aqueous liquid repellency of cotton fabrics before and after coatings, and Figure 6-3(e) lists the photos of the aqueous liquids on the surface of cotton fabrics. Cotton fabrics are not resistant to any aqueous liquids and all the liquids penetrate into the fibrous structure within several seconds. Due to the excellent hydrophobicity, the coated samples repel all the aqueous liquids for 600 seconds. The lower surface tension of coated surface usually plays an important role in the resistance to aqueous liquid and chemicals (Vazquez, 2005). The surface tension of aqueous liquids decreases from 59.0 to 25.4 dynes/cm with the increase of the alcohol/water ratio. As the surface tensions of all the coated fabrics are much lower than this, thus all the aqueous liquids are expelled and near-sphere droplets are shown in the photos of Figure 6-3(e).

6.3.2.4 Oil repellency

The oil repellency depends upon the surface tension of the coated surface. Uncoated cotton fabrics have a high surface tension to enhance the absorbency of liquids and oil, so that all the oils have penetrated into the fibrous structure as shown in Figure 6-4(a). The rubber membrane and fluoro-polymer have low surface tensions to reduce the surface tension of the coated cotton fabrics and thus enhance the oil repellency (Moiz et al., 2016).

As shown in Figure 6-4(a), all the coated cotton fabrics show excellent oil repellency and the oil droplets stay on the surface of fabrics for as long as 600 seconds. The oil with high surface tensions, such as castor oil 41.35 dynes/cm, paraffin oil 28.0 dynes/cm, n-hexadecane 27.3 dynes/cm, n-decane 23.8 dynes/cm and vegetable oil 26.8 dynes/cm are repelled by fluoro-polymers and their combination with rubber coated samples C-H. It is evident that the low surface tension of fluoro-polymers (16.2 -18.2 dynes/cm) brings the excellent oil repellency to the coated fabrics. Due to the closer surface tensions between n-heptane (19.8 dynes/cm) and the coated fabrics (18.2 dynes/cm), the n-heptane is not repelled by most coated fabrics except for sample E and H (16.2 dynes/cm), (Wang et al., 2011, Jarvis and Zisman, 1965). However, the difference in surface tension between TMMS (41.0 dynes/cm) (Lee, 1968) and n-heptane is high enough to grant the coated fabrics with repellency to n-heptane. On the other hand, rubber coated fabrics are not resistant to n-heptane and n-decane, as shown in Figure 6-4(a), and this is also due to their similar surface tensions. It is evident that fluoro-polymers coating has a very evident effect on oil repellency (Liang and Ruckenstein, 1996, Vazquez, 2005).

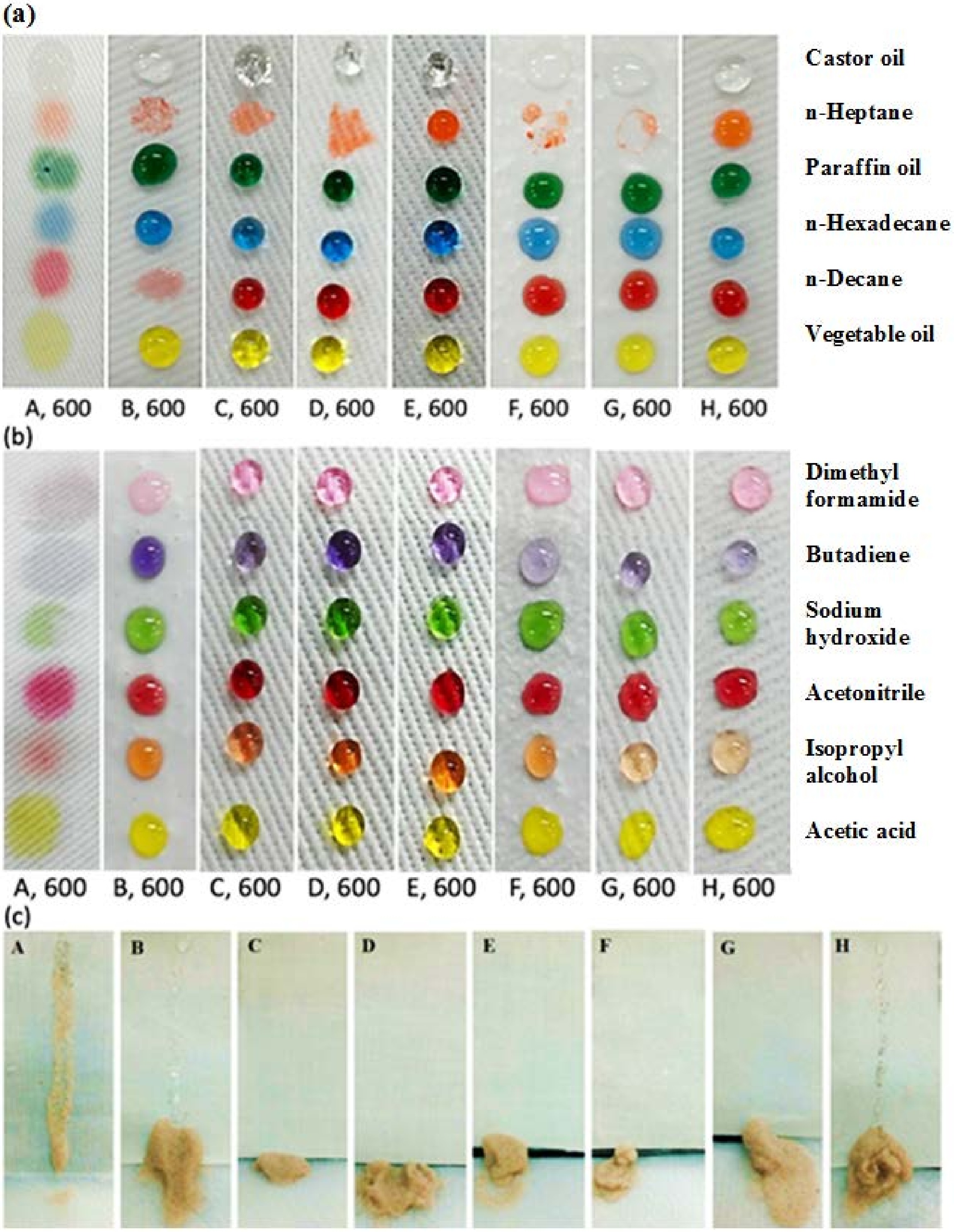

Figure 6-4: Protection of the as-coated cotton fabrics against oil (a), chemicals (b) and soil (c).

6.3.2.5 Chemical resistance

Table 6-1 illustrates the chemical resistance of cotton fabrics to different chemicals, and Figure 6-4(b) shows the photos the droplets of some chemicals on the all the samples. Cotton fabrics are not resistant to chemicals due to the wettability of cotton, and all the chemicals have been absorbed into the fibrous structure immediately with wet marks left on the surface of fabrics.

The coated cotton fabrics are resistant to most the chemicals except for dichloromethane, n-hexane and tetrahydrofuran. Due to the extremely low surface tension, fluoro-polymers are more effective in resisting chemicals than rubber. The coated cotton fabrics are resistant to most the chemicals except for dichloromethane, n-hexane, and tetrahydrofuran.

Fluoro-polymers coated cotton fabrics show chemical resistance to n-decane, sulphuric acids, n-heptane, triethylamine, and toluene, while that of rubber membrane coated is not resistant to these chemicals. Besides, the combination of rubber and fluoro-polymers is slightly more effective than fluoro-polymers. The combination of rubber membrane and fluoro-polymers has generated an omniphobic surface to display the optimized chemical resistance as compared to the uncoated surface of cotton fabrics (Pan et al., 2012, Moiz et al., 2016, Zeng et al., 2015, Moiz et al., 2017).

6.3.2.6 Soil resistance

Soil resistance has been measured to analyse the self-cleaning property of the coated fabrics. Uncoated cotton fabrics are not resistant to soil solution as the soil remains on the surface of fabrics as shown in Figure 6-4(c). The soil particles stain on the surface, making it hard to remove them from the surface of the fabrics. All the coated fabrics show excellent soil resistance with an excellent grade 5, and all the soil particles have been absorbed on the tissue papers as seen in Figure 6-4(c). The rubber membrane coated (sample B) and its combination with TMMS and phobol (sample H) are less resistant to soil with the grade 1. Together with the omniphobicity, the self-cleaning property brings the lotus effect to the coated fabrics (Zeng et al., 2015, Dhiman and Chakraborty, 2014, Chen et al., 2018), which will see a great application potential in protective clothing such as military uniform, mining uniform and outdoor sportswear.

6.3.3 Comfort

Comfort is another determining factor in developing performance textiles/protective clothing. The coated cotton fabrics show totally different comfort to the uncoated cotton fabrics as shown the results in Figure 6-5. The thermal resistance (Figure 6-5(a)) and water vapour resistance (Figure 6-5(b)) of fluoro-polymers coated cotton fabrics is not evidently different compared to that of the uncoated cotton fabrics. It is thus evident that the blocking of pores by the formed particles slightly affects the thermal conduction and moisture transfer (Li, 2017). However, once rubber membrane is coated onto the surface of cotton fabrics, the thermal and water vapour resistance are so different.

As seen from Figure 6-5(a), the rubber coated and the combined coated ones show lower thermal resistance. Besides, the water vapour resistance of these samples are much higher than the rest (Figure 6-5(b)). The thermal conduction, in this case, is mainly determined by the materials and the structure of the fabrics. Coating of rubber membrane has an evident blocking effect on the surface of cotton fabrics so, that the conduction of heat and transportation of moisture (permeability index) through the pores have been blocked.

Table 6-1: Chemical resistance (seconds) of uncoated and coated cotton fabrics

Sample code	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**Status**
Acetic acid	0	600	600	600	600	600	600	600	ER
n-Decane	0	0	600	600	600	600	600	600	ER
n-Hexadecane	10	600	600	600	600	600	600	600	ER
n-Heptane	0	0	39	540	600	120	147	600	ER
Paraffin oil	0	600	600	600	600	600	600	600	ER
Sulphuric acid	0	0	103	105	107	600	600	540	LR
Isopropyl alcohol	0	600	600	600	600	600	600	600	ER
n-Hexane	0	0	0	0	0	0	19	20	NR
Sodium hydroxide	0	600	600	600	600	600	600	600	ER
Tetrahydrofuran	0	0	0	0	0	18	0	0	NR
Triethylamine	0	10	535	26	10	540	23	45	LR
Methanol	0	10	600	600	600	186	570	600	ER
1, 4 butadiene	0	600	600	600	600	600	600	600	ER
Dimethylformamide	0	600	600	600	600	600	300	600	ER
Acetonitrile	0	600	600	600	600	600	600	600	ER
Toluene	0	0	600	0	0	600	0	0	NR
Dichloromethane	0	0	0	0	0	60	10	15	NR
Castor oil	0	600	600	600	600	600	600	600	ER

Note: ER: excellent resistance; LR: limited resistance; NR: not resistance.

The water vapour resistances of these fabrics are thus higher. However, the thermal conduction is also determined by the materials of the fabrics, and the coated rubber membrane has a higher thermal conduction capability to overweight the blocking of thermal conduction through the fibrous structure (Rasid, 2017, Li, 2017). The overall thermal resistance of these fabrics are thus lower than the uncoated and fluoro-polymers coated ones.

The moisture management property of cotton fabrics has been changed after the coating. The uncoated cotton fabrics show similar MMT profiles from the top and bottom surfaces, as shown in Figure 6-5(c). Cotton fabrics have excellent wettability, and thus a droplet of water can easily penetrate and spread on both sides of the fabrics. However, the coated fabrics show totally different profiles with a droplet of water on the top surface and nothing on the bottom surface. This is due to the excellent superhydrophobicity of the coating that prevented the water from penetrating and spreading into the fabrics.

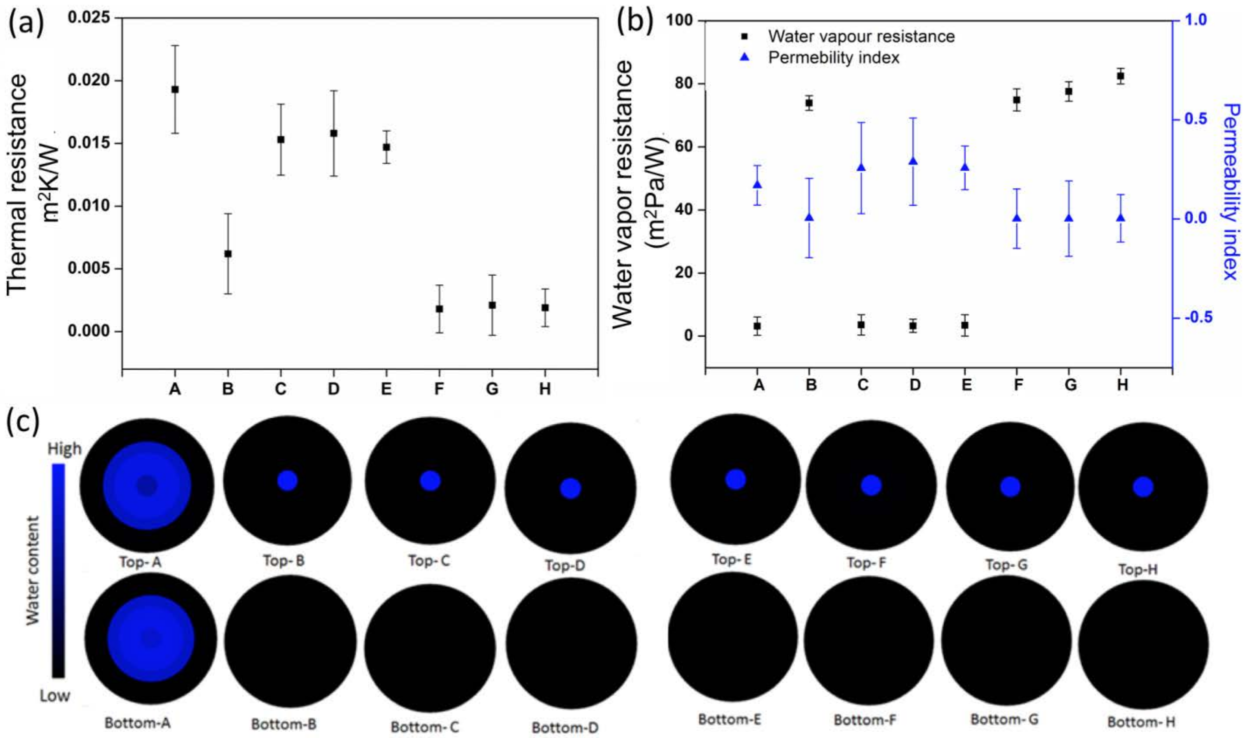

Figure 6-5: Comfort analysis of the as-coated cotton fabrics: (a) Thermal resistance; (b) Water vapour resistance with permeability index; (c) Moisture management test (MMT) profiles.

6.4 Summary

In the summary, a durable and superomniphobic surface was developed by the pad-knife-pad-cure coating of rubber membrane and fluoro-polymers. The coating brought a thin membrane with a low surface tension and many particles to increase of surface roughness. The coated cotton fabrics were more rigid with a higher bending length and were stiffer with higher KES values of surface friction and roughness. The coating resulted in a cross-linked network due to the strong bonding between the CH_3 groups of rubber and the CF_2 groups of fluoro-polymers. The coated cotton fabrics showed a water contact angle of around 140-150°, and the superhydrophobicity was durable against different cycles of laundering and pilling. The coated fabrics repelled 80-90% of water with air permeability of around 70%, and all the aqueous liquids with different water/alcohol ratios were repelled from the coated surface. The coated cotton fabrics showed excellent oil repellency and chemical resistance as most oils and chemicals were repelled from the surface. However, oil and chemicals with closer surface tension to the coated surface were not resistant. The coated fabrics also showed soil resistance without staining of sands on the surface. Due to the existence of the coated layers, the coated fabrics showed decreased thermal resistance and increased water vapour resistance with quite different MMT profiles compared to the uncoated fabrics.

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7 COMPARATIVE STUDY OF IMP TECHNOLOGY, PAD-KNIFE COATING AND LAMINATED MEMBRANE FABRICS

7.1 Introduction

Plasma technology uses different gases such as nitrogen, oxygen and helium to increase the hydrophobicity and surface roughness of fabrics while the physical properties of the treated fabrics are well preserved (Asadian et al., 2017). Surface modification with plasma technology brings the fabric higher liquid entry pressure and an air gap between the membranes. The plasma treatment was also used in combination of chemical vapour deposition of nanoparticles from fluoro-polymers, and the combined method was used to remove toxic gases. However, these methods are based on multi-step and not suitable for hydrostatic pressure resistant (DeCoste and Peterson, 2013). Plasma treatment with fluoro-polymer chain C_8 was found to better resist oil, acids, UV light with the self-cleaning property. However, the superhydrophobicity and oleophobicity were not effective after the mechanical action of laundering and abrasion, which meant the coating was not stabilised on the surface of fabrics to exhibit durability. Therefore, the long chain of fluoro-polymer C_8 is not suitable to be used as the safer polymeric coating (Wang et al., 2011). Plasma surface modification combined with polyvinylidene fluoride (PVDF) membrane were used to develop superhydrophobic and omniphobic surface by the electrospinning (Liao et al., 2013). PVDF and fluoro-silane polymer were applied on fabrics by dip coating, and the coated fabrics were further treated by vacuum plasma to enhance the superhydrophobicity, oleophobicity and self-healing with durability against laundering and abrasion.

Plasma treatment always requires specific equipment that adds the cost of the application of the technology (Zhou, 2013). Plasma treatment usually has to be applied under a specific pressure, and a lower vacuum pressure does not guarantee the good hydrophobicity of the fabric surface (Hossain, 2006). Besides, the plasma treated fabrics cannot resistant organic contaminations waste (Chul Woo et al., 2017, Keating et al., 2018). Argon plasma treatment was used with lactic acids to increase the dyeing efficiency, biodegradable and antibacterial activity, but the process was very hard to control in order to obtain the dark shade of the dyeing (Wang et al., 2017).

The IMP plasma Pi_2 technology (IMP) is a liquid repellent functionalising technique which consumes a low level of energy with little wastes created. The technology is available in two styles, namely the elite force Wpi technology that provides ultimate resistances with comfort and the shielding force that provides fire resistance protection. IMP is an invisible technology with the visible results of water repellency or self-cleaning properties (USA, 2010). It brings a nanolayer which is 1000 times thinner than a human hair to the treated fabrics for protection. The layer is light weight, breathable, water resistant and less wettable with durability, and it provides high- level resistance to water, chemical warfare agents and blood borne pathogens.

IMP treated products are solvent resistant, and they don’t absorb any dirt particles from mud or car splashing. It is widely used to develop protective coating with lightweight, breathability, protection and durability. IMP technology has been adopted to provide the ultimate protection with comfort for policemen, paramedics and soldiers. It creates the robust superhydrophobic surface for commercialisation and research with application in outdoor clothing, sports life science, food packaging industry, medical devices, biomaterials, filtration and energy (Pankaj, 2014, Holme, 2007). Military force uses IMP technology to develop military garments with excellent resistance to chemical warfare agents, oil and staining.

Eco-friendly C_6 perfluorinated acrylic copolymer and PDMS silicone polymer were used to develop excellent water-resistant coating with durability after laundering and abrasion stress, but its hydrostatic pressure stability was only 2.56 kPa (Zahid et al., 2017). Pad-knife-pad coating methods were developed to coat WPU, TPU and PDMS-TMS on cotton and polycotton fabrics to enhance the resistance to water, oil and chemicals. WPU membrane was less air permeable as compare to the TPU polymeric coating, and TPU polymeric coating showed better comfort (Moiz et al., 2016, Moiz et al., 2017). This Chapter focuses on the comparison between the pad-knife-pad coated fabrics with the IMP treated fabrics and industrial fabrics, contributing a critical analysis of the results which will benefit the further development of chemical protective clothing.

7.2 Experimental

7.2.1 Materials

Different fabrics were used and the properties of each fabric were displayed in Table 7-1. A non-ionic detergent of the octylphenol ethoxylate was sourced from the Dow Corning Pty Ltd, Australia. ICB Fix Tubicoat Iso-cyanates and waterborne polyurethane (WPU, Tubicoat membrane 1665, in paste form) were purchased from CHT Pty Ltd, Australia. A mixture of 35% polydimethylsiloxane (PDMS) and 35% trimethylated silica (TMS) was purchased from Dow Corning Pty Ltd, Australia. Invadine PBN, Kinttex® FEL, Phobotex RSH and Olephobol ® CP-C were purchased Huntsman Singapore Pty Ltd. Hexadecane and n-Decane were purchased from Sigma Aldrich Pty Ltd, Australia. Mineral oil was purchased from Johnson and Johnson Pacific Pty Ltd, Australia. Acetonitrile, Isopropyl alcohol and Dichloromethane (Ana-R) were purchased from BDH Limited Poole, England. Sulphuric Acid (98%) was purchased from RSL LAB SCAN Ltd, Thailand. Dimethylformamide was purchased for Merck, Germany. Sodium hydroxide was purchased from Chem Supply Pty Ltd, Australia.

7.2.2 Preparation of Fabrics

In IMP treatment, the fabrics were first scoured in an MCS mini jet dyeing vessel with o.1 w/v octylphenol ethoxylate solution in water and a liquor ratio of 20:1, for 30 minutes and scoured by caustic soda at 90°C for 1 hour. Scoured fabrics were rinsed in warm water and then in cold water. Rinsed fabrics were left overnight for hanging dry in an ambient environment. After scouring the fabrics were cut into A4 size for the IMP treatment at the Global Defence Solutions Pty Ltd, Australia. The IMP machine (Figure 7-1) has the capacity of about 400 litres with the dimension of 560 mm.

The specimens were placed into the chamber, and a low vacuum pressure was achieved to create plasma inside the chamber. The exposure time for each specimen was five minutes. The IMP treated fabrics were denoted as OG, SG, PB and RB with details listed in Table 7-1

LPB and LRB used as industrial fabrics. WPTC and WOC fabrics were prepared by the pad-knife-pad-cure method as described in Chapter 4.

Table 7-1: Specification of fabrics used.

Fabrics	**Construction**	**Fabric weight (g/m²)**	**Fibres**
Olive Green (OG)	2/2 twill	80	100% polyester
Safety Gold (SG)	2/1 twill	220	45% Aramid, 32% FR viscose, 17% nylon
Paris Blue (PB)	plain weave	155	50% Nomex, 50% FR viscose
Royal Blue (RB)	plain weave	90	100% polyester
Lines Paris Blue (LPB)	plain weave face, PTFE membrane, plain weave polyester lining	190	100% polyester (industrial fabrics)
Laminated Royal Blue (LRB)	plain weave with laminated membrane backside	60	100% polyester (industrial fabrics)
WPU-PDMS-TMS (WPTC)	RMIT University developed the blended cotton fabric with camouflage printing.	182	80:20 % cotton and polyester with camouflage printing
WPU-Olephobol (WOC)	RMIT University developed the blended cotton fabric with camouflage printing.	182	80:20 % cotton and polyester with camouflage printing

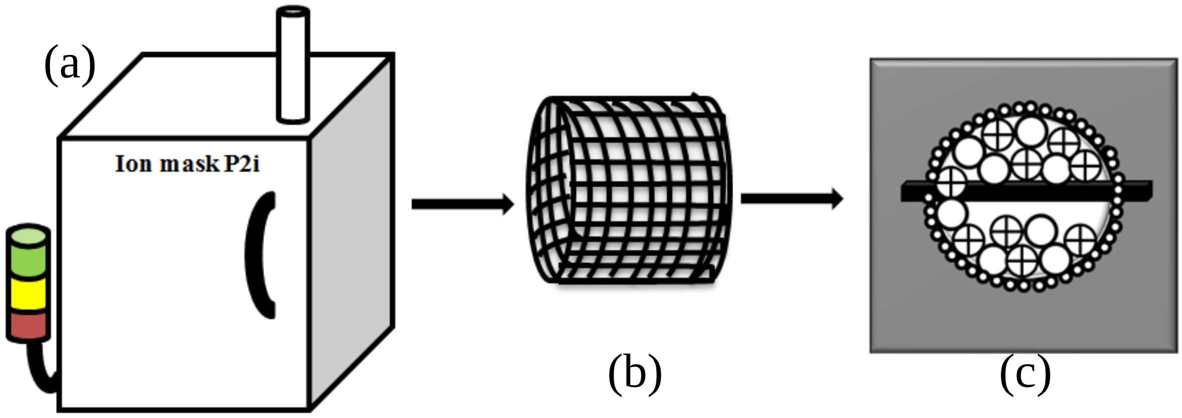

Figure 7-1: The process of IMP treatment: (a) ion mask chamber; (b) ionisation of polymerisation; and (C) ions attached with the fabrics surface.

7.3 Result and discussion

In the plasma treatment, the low vacuums pressure was created to allow the energized polymer molecules to pass through the surface of fabrics with fewer amounts of fluorocarbon chemicals.

Meanwhile, polymers molecules were ionized in the chamber, creating active binding sites for the micro- or nano-level coating penetrating in between the fibres.

7.3.1 Morphology of fabrics

Figure 7-2 shows the surface morphology of the IMP treated fabrics and the coated fabrics with insets of the untreated/uncoated fabrics. The untreated fabrics show smooth and clean surfaces. The IMP treatment has formed a thin layer of polymeric coating on the surface of OG fibres with surface roughness and many particles aggregated, as shown in Figure 7-2(A). For IMP treated SG fabrics, accumulated particles can be observed from the surface of fibres Figure 7-2(B). The surface of PB fibres have been severely etched and damaged after the IMP treatment, resulting in a rough and uneven morphology with particles in Figure 7-2(C). Similarly, the RB fabrics show blister and hills on the surface after IMP treatment, as shown in Figure 7-2(D) (Wróbel et al., 1978, Caschera, 2014). The damaged surface with particles on fibres is due to the degradation and ionisation of polymers in the IMP treatment. The plasma treatment energised the polymer molecules and deposited them onto the fibre surface with low surface energy. The rough surface with particles was then formulated.

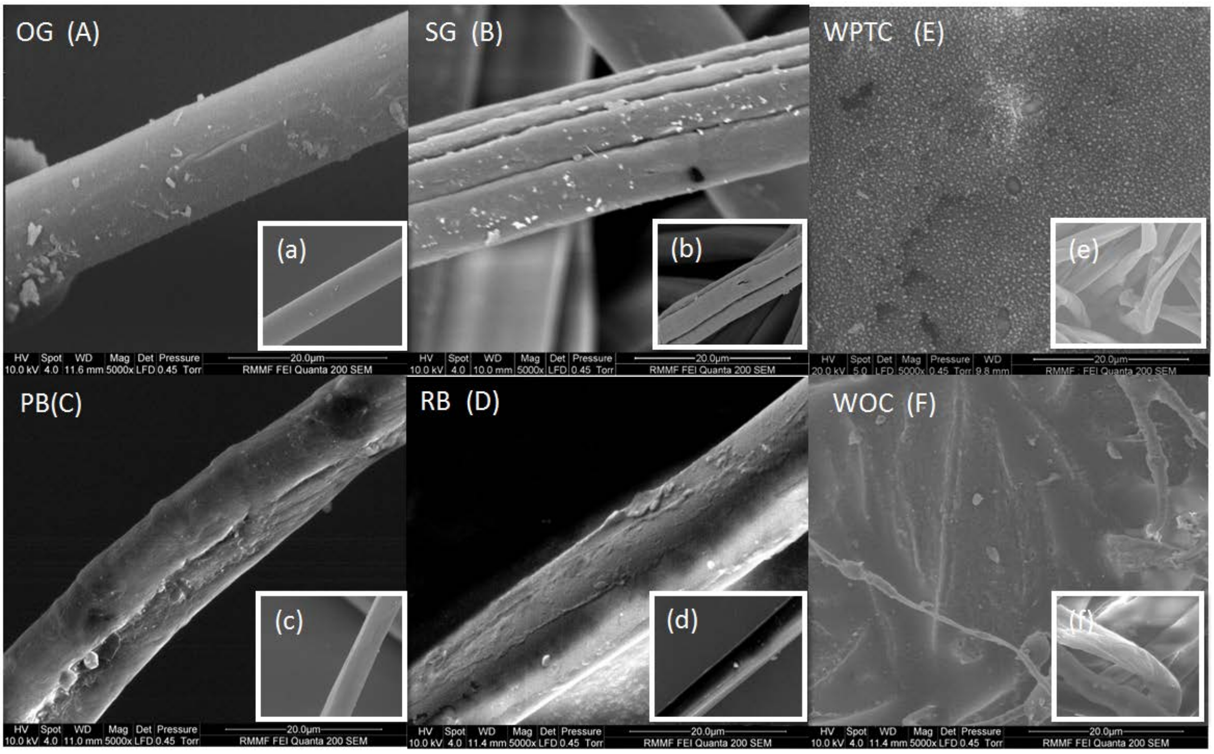

Figure 7-2: SEM images of IMP treated and pad-knife-pad coated fabrics (A-F: treated fabrics; insets a-f: untreated fabrics).

For comparison, the surface morphology of coated fabrics is shown in Figure 7-2(E-F). The WPTC (WPU membrane plus 8% PDMS-TMS) coated fabrics have been covered with a whole layer of the membrane of WPU with surface roughness and many particles from PDMS-TMS. The WOC (WPU membrane plus oleophobol) coated fabrics indicate an uneven surface with roughness, and the fibrous structure of fabric has been half covered by the coated layer.

7.3.2 FTIR spectra

Figure 7-3 shows the FTIR spectra of the IMP treated and pad-knife-pad coated fabrics. The spectrum of OG fabrics shows the functional groups of CH stretching and bending at 2900 cm^{-1} and 2966 cm^{-1}, respectively. The C-C vibrational bonding in the benzene ring is shown at around 2250-1650 cm^{-1}. The carbonyl group and OH group appears at 1709 cm^{-1} and 3350 cm^{-1}, respectively. The anhydride group appears at 1958 cm^{-1} and C=O strong bonds present at 1757 cm^{-1} with asymmetric stretching. After the treatment with IMP, a number of visible dominating peaks shifted slightly in the spectrum with large parks at 1734 cm^{-1} to 650 cm^{-1} due to the presence of carbonyl group from OG fabrics.

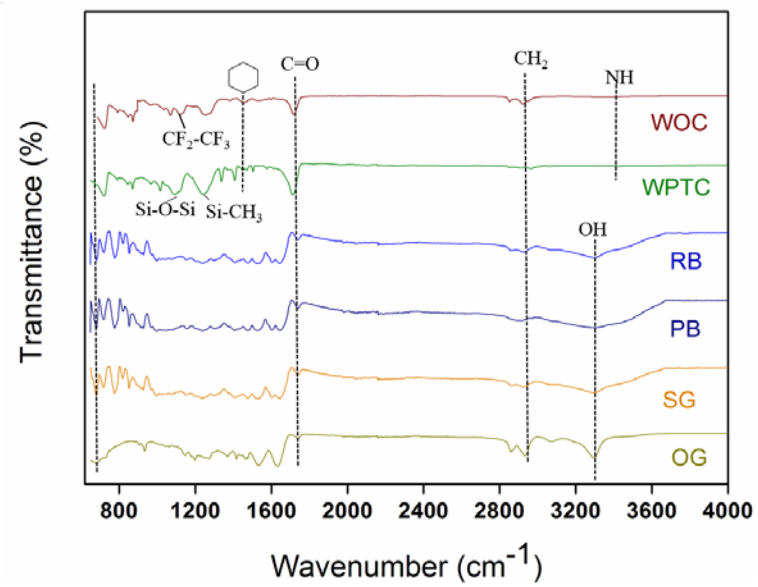

Figure 7-3: FTIR spectra of IMP treated and pad-knife-pad coated fabrics.

The spectra for IMP treated fabrics (OG-RB) show the changes in the functional groups of C=O and OH. There is a reduction in the OH group that contributes to the hydrophobicity of the surface. No further changes in the chemical components have been observed after the treatment, because the IMP technology is used to change the surface and structures of fabrics slightly (Caschera, 2014).

WPTC coated fabrics show the characteristic peaks of WPU at 2935 cm^{-1} and 1713 cm^{-1}, corresponding to the CH_2 and C=O groups. In addition, the characteristic bands of PT, such as the Si-O-Si and the Si-O-C overlapped bands can be seen in the spectrum. Similarly, the presence of TMS can be noted at 1251-1257 cm^{-1} due to the copolymerization reaction between the two polymers (Moiz et al., 2016). WOC coated fabrics exhibit the spectrum with similar functional groups of NH, CH_2, C=O and visible peak of fluoro-polymers (CF_2-CF_3) between the 1338 cm^{-1} to 1208 cm^{-1}, resulted in the hydrophobic surface on the fabrics.

7.3.3 Superhydrophobicity and durability

IMP treatment has brought excellent superhydrophobicity to fabrics, as shown in Figure 7-4. The IMP treated fabrics show the water contact angle of around 160^o. Whereas, the industrial fabric LPB and pad-knife-pad coated fabrics are hydrophobic with the water contact angle around 130-140^o. The other industrial fabric LRB is hydrophilic with a water contact angle of 86^o. The superhydrophobicity is due to the generated rough surface with an extremely low surface tension by the IMP treatment. LRB has a laminated layer at the back side of fabric; however it can absorb oil and chemical from the front side.

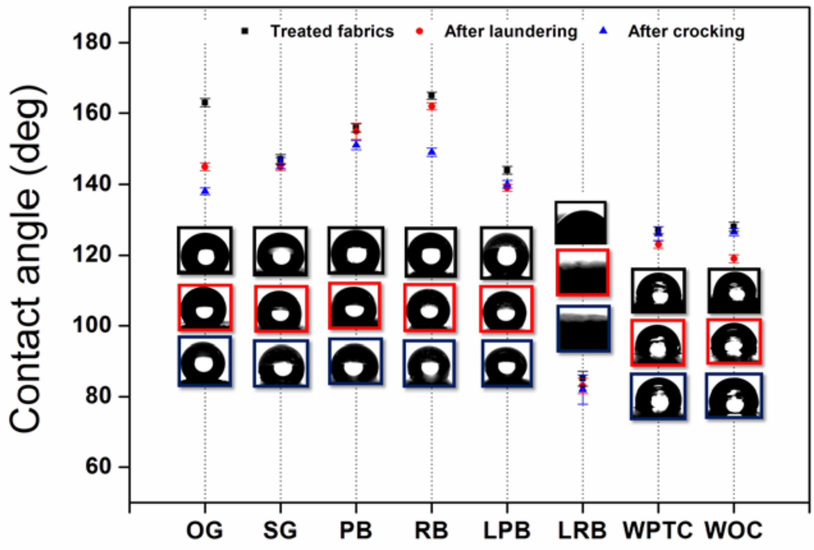

Figure 7-4: The water contact angle of all the fabrics before and after laundering and crocking.

The durability of the hydrophobic surface against laundering and crocking has been the issue for developing protective clothing. The weak bonding between the coated layer and the substrate can break easily after rubbing (Roe and Zhang, 2009). IMP treated fabrics SG, PB and RB have very good durability against washing as the water contact angle only decreases by 2-3° after washing.

At the same time, the IMP treated fabric OG is much less durable as the water contact angle decreases by 18° after laundering. IMP treated fabrics SG and PB have excellent durability against crocking with a 2-4° decrease in the water contact angle. However, OG and RB are less durable with the reduction of 13-25° in water contact angle after crocking. Industrial fabrics LPB and LPB show acceptable durability against washing and rubbing with the reduction of 2-5° in water contact angle. LRB is less durable due to the laminated layer on its backside. WPTC coated exhibits excellent durability with only 1° reduction after laundering cycles and crocking (Moiz et al., 2016). WOC coated fabrics retain the hydrophobicity with reduction of 9° and 2° after laundering and crocking, respectively.

The durability of the hydrophobic surface is crucial in maintaining long-lasting properties of the protective garments (Zeng et al., 2015). The strong bonding sites always play a key role in maintaining the durability of hydrophobic surface. The excellent durability of IMP treated and pad-knife-pad coated fabrics are due to the strong bonding between the formed layers and the fabrics.

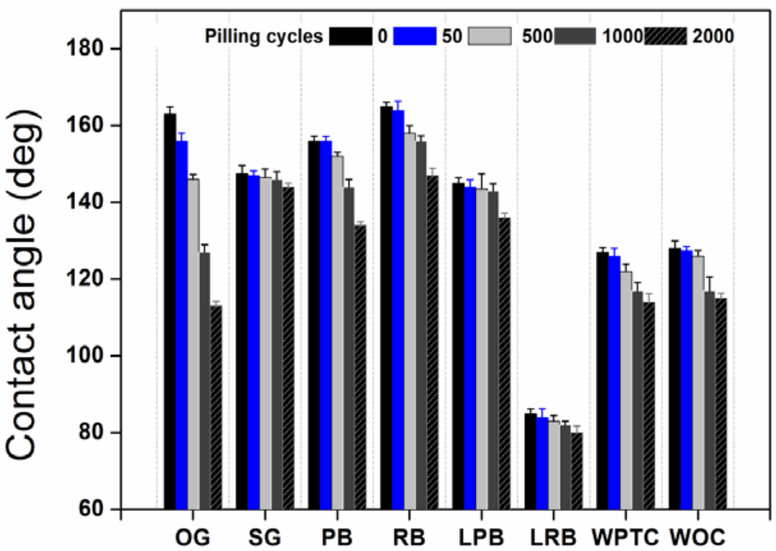

Figure 7-5: The water contact angle of all fabrics after different cycles of pilling.

All the fabrics were subject to different cycles of pilling to assess the durability of the surface against mechanical action (Figure 7-5). The water contact angle of all the fabrics decreases slightly after 50-500 cycles of pilling followed by evident drops after 1000 cycles. However, the SG and LRB show changes in water contact angle even after 2000 cycles of pilling. The superhydrophobicity can be well preserved after different cycles of pilling as the reduction for most fabrics is within 20°. It is noted that OG shows a very evident drop in water contact angle after different cycles of pilling, indicating poor durability against the mechanical action. Overall, the IMP treated fabrics except for OG, industrial fabrics and pad-knife-pad coated fabrics have the strong surface with durability to withstand different cycles of pilling.

7.3.4 Aqueous liquid repellency

IMP treated fabrics have low surface tensions to increase the repellency to aqueous liquids of water and alcohol mixtures with different ratios (2-40%). The surface tension of the treated fabrics such as OG, SG, PB and RB fabrics is within the range of 59-24 dynes/cm. Figure 7-6 shows the photos of aqueous liquids on each fabric after 600 seconds. It is obvious that the IMP treated fabrics are resistant to all the aquous liquids as shown in Figure 7-6. The industrial fabrics LPB and LRB show no resistannce to all types of aqueous liquids, and the liquids penetrate into the fibrous structure within a second. This is due to the similar surface tension between the liquids and the industrial fabrics. WPTC and WOC fabrics show excellent resistance to all types of aqueous liquids. The coated surface of WPTC and WOC with lower surface tensions repels the liquid mixtures with higher surface tensions (Moiz et al., 2016). IMP treated fabrics have a superhydrophobic surface with super repellency and self-cleaning properties (Vazquez, 2005).

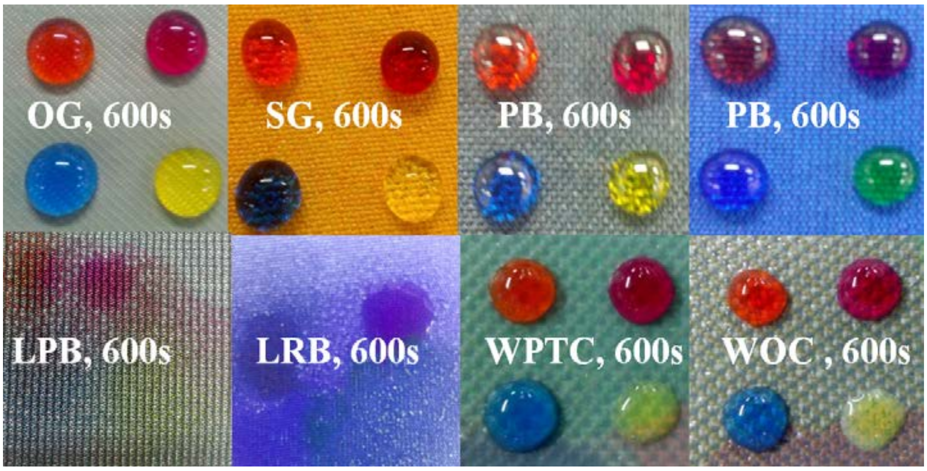

Figure 7-6: Aqueous liquid repellency of IMP treated fabrics, WPTC and WOC coated fabrics and industrial fabrics (Water/alcohol Composition ratio: Orange 98/2; Red 90/10; Blue 80/20; Yellow 60/40, respectively).

7.3.5 Oil repellency

The surface with oleophobicity and superhydrophobicity plays a key role in protection against oil and water. The untreated fabrics were not resistant to all types of oil due to their hydrophilic nature. After the IMP treatment, the surface tension and energy of fabrics were reduced at the same time, resulted in the excellent oil repellency. As shown in Figure 7-7, the IMP treated fabrics repel all kinds of oil with the droplets of oil staying on the surface of fabrics like balls. Table 7-2 lists the time for oil to be absorbed into the fabrics as another way to show the oil repellency. WPTC and WOC are resistant to all types of oil due to the lower surface tension of the coated surface (Moiz et al., 2016, Wang et al., 2011). However, the droplets of oil on the surface of the coated fabrics are in the shape of semi-sphere. It is apparent that IMP treatment brings better oil repellency to fabrics than the pad-knife-pad coating. In contrary, industrial fabrics LPB and LRB are not resistant to all types of oil.

Table 7-2: Oil repellency in different time intervals (seconds).

Sample	**Castor oil**	**Vegetable oil**	**Paraffin oil**	**n-Hexadecane**	**n-Decane**	**n- Heptane**
OG	600	600	600	600	600	600
SG	600	600	600	600	600	44
PB	600	600	600	600	600	600
RB	600	600	600	600	600	600
LPB	136	0	0	0	0	0
LRB	94	50	10	60	20	0
WPTC	600	600	600	600	600	600
WOC	600	600	600	600	600	600

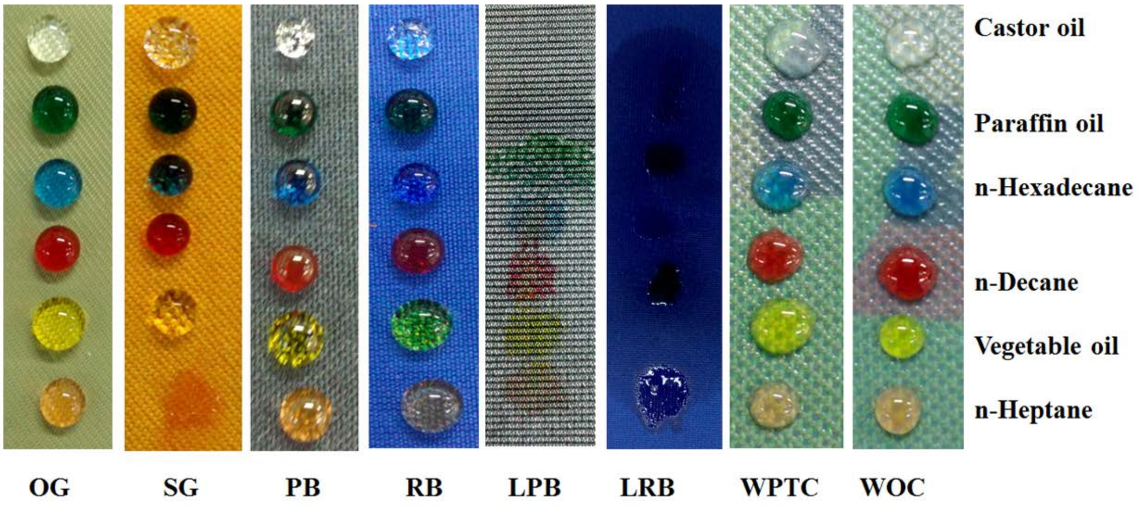

Figure 7-7: Oil repellency of IMP treated fabrics, WPTC and WOC coated fabrics and industrial fabrics.

7.3.6 Chemical resistance

Chemical stability is a very important factor in protective clothing for safety. Military uniforms with chemical resistance can protect skin from being attacked by chemical agents and save lives.

Shows the example of chemical resistance to sulphuric acid for all the fabrics, and apparently, all the fabrics are not resistant to the strong acid and burns on the surface of fabrics can be observed. Table 7-3 lists the chemical resistance of all the fabrics to a range of chemicals. Industrial fabric LRB has no chemical resistance and all the chemicals penetrate the fabric swiftly, whereas the other industrial fabric LPB resists some of the chemicals as shown in Table 7-3. LPB has excellent resistance to isopropyl alcohols, acetic acid, and sodium hydroxide, 1-4 butadienes, dimethylformamide and acetonitrile for 600 seconds as seen from the data.

Table 7-3: Chemical resistance of all the fabrics.

Sample	OG	SG	PB	RB	LPB	LRB	WPTC	WOC	Status
Acetic acid	600	600	600	600	600	0	600	600	ER
Sulphuric acid	276	201	152	212	10	10	422	545	LR
Isopropyl alcohols	600	600	600	600	600	0	600	600	ER
n-Hexane	0	0	0	0	0	0	15	13	NR
Sodium hydroxide	600	600	600	600	600	0	600	600	ER
Tetrahydrofuran	446	550	147	489	0	0	125	174	ER/LR
Triethylamine	133	77	0	60	0	0	212	298	LR/NR
Methanol	600	600	600	600	489	0	235	600	ER
1,4 butadiene	600	600	600	600	600	0	600	600	ER
Dimethylformamide	600	600	600	600	600	0	600	600	ER
Acetonitrile	600	600	600	600	600	0	515	473	ER
Toluene	600	600	600	600	0	0	180	600	ER
Dichloromethane	276	201	152	212	0	0	24	10	LR

Note: ER: excellent resistance; LR: limited resistance; NR: not resistance.

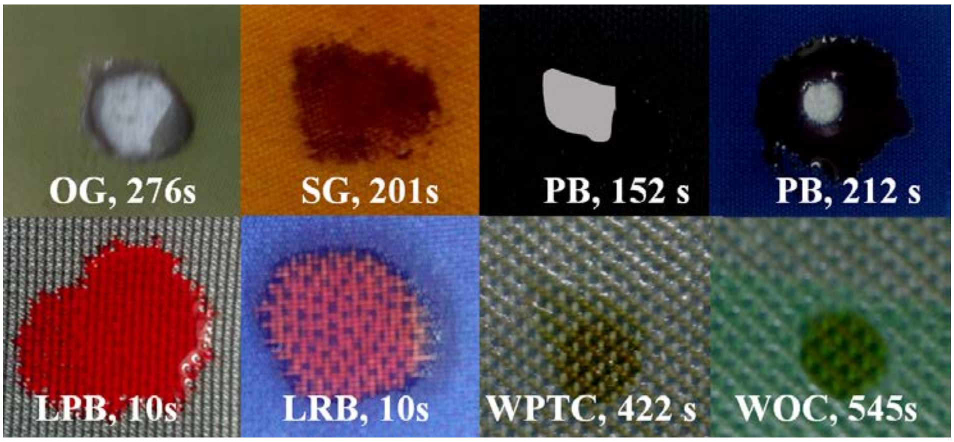

Figure 7-8: **Chemical resistance to sulphuric acid of IMP treated fabrics, WPTC and WOC coated fabrics and industrial fabrics.**

IMP treated fabrics are not resistant to n-hexane and the droplet penetrates into the fabrics immediately. The IMP treated fabrics show limited resistance/no resistance to triethylamine with less than 120 second and limited resistance to dichloromethane and sulphuric acid with 152-276 seconds. Other than these, the IMP treated fabrics show excellent resistance to most of the chemicals for 600 seconds due to the low surface tension of their surface.

WPTC and WOC show excellent resistance to most of the chemicals and limited resistance to n-hexane, tetrahydrofuran and dichloromethane due to their similar surface tension (Moiz et al., 2016, Pan et al., 2012, Zeng et al., 2015).

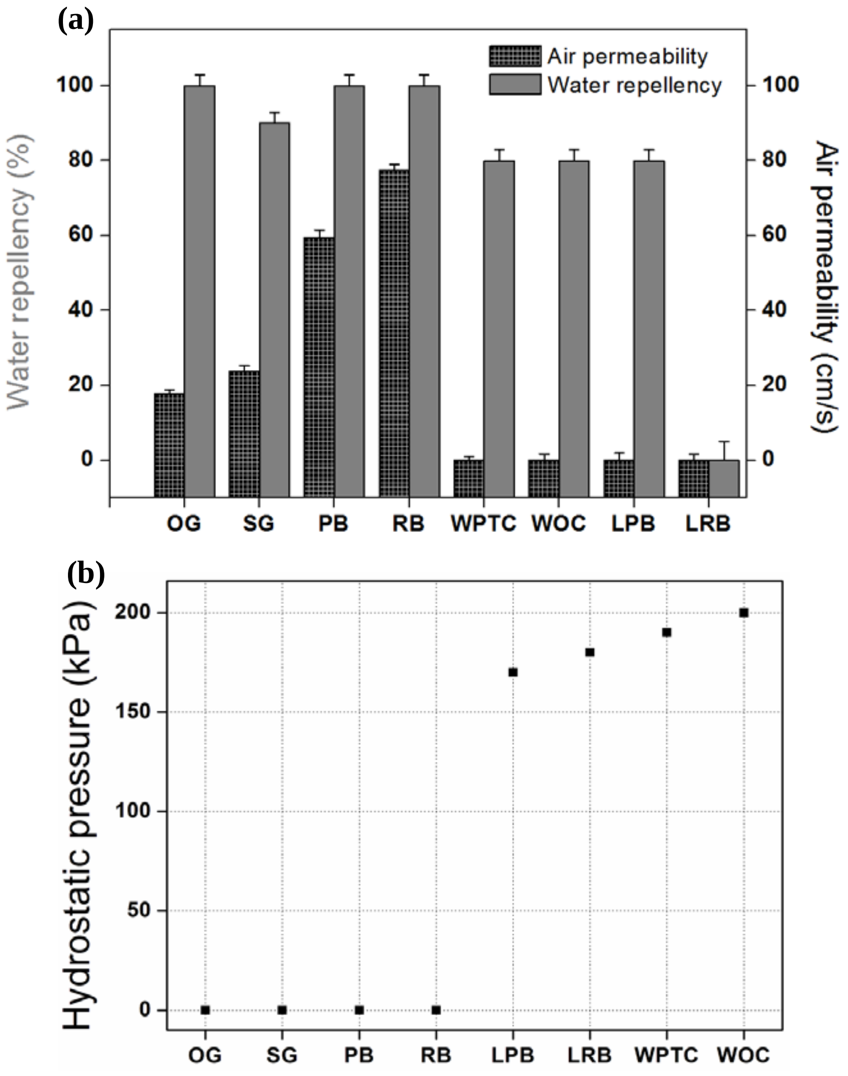

Figure 7-9: Water repellency, air permeability (a) and hydrostatic pressure (b) of all the fabrics.

7.3.7 Air permeability, water repellency and hydrostatic pressure

Figure 7-9(a) shows the air permeability, water repellency and hydrostatic pressure of all the fabrics. It is evident that both coating and IMP treatment affect the air permeability of fabrics, as most of the coated/treated fabrics show very low air permeability. All the fabrics except for LRB show excellent water repellency as 80-100% water is repelled. The industrial fabrics and the coated fabrics show excellent hydrostatic pressure as shown in Figure 7-9(b). The reason for this is probably due to the uniform membrane on the surface of fabrics that can withstand the pressure to a much higher level. In contrary, the IMP treated fabrics have extremely low hydrostatic pressure. As the plasma treatment does not bring a whole uniform membrane to the surface of fabrics, the capability of the surface to prevent hydrostatic force is very weak.

7.4 Summary

IMP is very simple and unique techniques to functionalise the surface of fabrics with superhydrophobicity. The IMP treated fabrics show the rough surface with particles, but the fibrous structure has been well preserved after the treatment. IMP treated fabrics show higher superhydrophobicity than industrial fabrics and pad-knife-pad coated fabrics, and the durability of the hydrophobic surface is excellent. The repellency against oil, aqueous liquids, and chemicals of IMP treated fabrics and pad-knife-pad coated fabrics are more or less similar. The hydrostatic pressure of IMP treated fabrics is extremely low, whereas that for coated fabrics and industrial fabrics is very high. The simple method of the pad-knife-pad coating has brought the omniphobic surface to fabrics with excellent hydrostatic pressure, which has a high potential in developing protective clothing for military force and/or industrial applications.

8 CONCLUSION AND FUTURE RESEARCH

8.1 Summary

Chemicals create severe risks and danger to civilian and military. Research base investigation has determined the effects of chemicals and the comfort properties of protective clothing. Protective clothing is available in multilayered, yet the garments are heavy and uncomfortable to wear. There is a need to develop simple methods of polymeric coating and repellent to enhance the protection of chemical, towards low weight and comfortable wearing clothing in the war zone. As a result, the protective clothing from cotton or cotton-based fabrics might be wearable, especially on the battlefield. Solider and civilian surveyed would be more comfortable and would be provided with better protection against water, liquids, oils, and chemicals.

In this research, the widely used padding-knife coating-padding-curing (pad-knife-pad) coating technology was adopted to develop multiple protective layers from waterborne polyurethane (WPU), polydimethylsiloxane (PDMS) and trimethylated silica (TMS). The chain of PDMS-TMS cross-linked and combined with the backbone chain of WPU to form a cross-linked network between the two polymers on the surface of cotton fabrics. Morphology study revealed that a uniform membrane of WPU with particles was formed on the surface. Due to the low surface tension of the coated layers, the coated cotton fabrics showed a water contact angle of 155°. The coating showed excellent durability after laundering and crocking, and this was due to the strong bonding within the coated layers and between the coating and the fabrics. A combination of WPU-PDMS-TMS (WPT) coating on cotton fabrics greatly enhanced the repellency and protective properties, as the coated fabric showed excellent repellency to water, oil, aqueous liquid and hydrostatic pressure. Chemical resistance was brought to cotton fabrics after the coating, and the WPT coated cotton fabrics showed better chemical resistance than WPU coated and 8% PT coated. After exposure to strong ultraviolet light on WPU membrane, the excellent resistance to chemicals and the hydrophobic surface were unchanged. The air permeability of WPT coated cotton fabrics was much lower than that of cotton fabrics due to the continuous defect-free WPU film that affected the pore size and blocked the pores of fabrics.

Careful selection of the coated materials has proven to be the determining factor of the protection and comfort of the coated fabrics. Using the same pad-knife-pad coating method, a soft, flexible, highly durable, comfortable, and versatile protective surface from the combination of thermoplastic polyurethane and PDMS-TMS was formed on polycotton fabrics. Morphology study revealed that a thin layer was formed on the surface of fibres rather than a uniform membrane on the fabrics. The cross-linked network from TPU-PDMS-TMS (TPT) provided flexible and soft segments with low surface energy siloxane groups to the polycotton fabrics. The superhydrophobic surface was formed on the coated fabrics with a water contact angle of up to 155°. Excellent durability of the coating was noticed when the coated fabrics were subject to different cycles of laundering and crocking, and this was due to the recrystallization of the long chains of the methyl groups of the PDMS and Si–OCH_3 bonding imparted between the substrate and the TPT coating. Similar to WPT, the TPT coating showed excellent repellency against water, oil, aqueous liquids and chemicals, and the protective capacity was not heavily affected even when the coated fabrics were subject to tensions. The TPT coating showed better comfort than WPT, even though the air permeability and water vapour permeability were deteriorated to some extent due to the blocking of the porous fibrous structure of polycotton fabrics. The thermal resistance of the coated polycotton fabrics was enhanced due to the trapping of static air within the fabric structure by the coated layers. The moisture management properties of the coated fabrics were totally different. TPU coating enhanced the water spreading capacity on the surface of polycotton fabric but deteriorated the water transport capacity. The TPT coated fabrics exhibited water droplets on their surface and showed poor moisture management capacity.

A combination of silicone rubber and environmentally friendly fluoro-polymers was found to be effective in generating superomniphobic surface on cotton fabrics by the same pad-knife-pad coating method. The coating resulted from thin membrane with roughness surface and particles on the fabrics, and the coated fabrics were more rigid with a higher bending length, and were stiffer with higher KES values of surface friction and roughness. A cross-linked network with a very low surface tension was formed through the strong bonding between the CH_3 groups of rubber and the CF_2 groups of fluoro-polymers, resulting in a durable superhydrophobic surface with the water contact angle of around 140-150°. The coated fabrics showed excellent repellency to water, aqueous liquids, oil and chemicals, and staining resistance of the coated fabrics to soil was noticed as well. The coated fabrics showed decreased thermal resistance and increased water vapour resistance with quite different MMT profiles after coating.

A careful comparison between the plasma treatment (IMP technology) and the pad-knife-pad coating was contributed with industrial fabrics as references. The IMP treated fabrics showed the rough surface with particles on fibres with the fibrous structure well preserved, whereas a membrane was usually formed on the pad-knife-pad coated fabrics. IMP treated fabrics showed higher superhydrophobicity than industrial fabrics and pad-knife-pad coated fabrics. The durability of the hydrophobic surface on all the fabrics was excellent due to the strong bonding between the functional layers and the fabrics. Both the treated and coated fabrics showed similar repellency against water, oil, aqueous liquids and chemicals. However, the hydrostatic pressure of IMP treated fabrics was extremely low, whereas that for the coated fabrics and industrial fabrics was very high.

With the superomniphobic surface brought to fabrics with excellent protection capacity and durability together with strength against hydrostatic pressure, the simple method of the pad-knife-pad coating has a high potential in developing protective clothing for military force and/or industrial applications.

8.2 Scope and limitations

The pad-knife-pad coating method was demonstrated in the chemical laboratory with the size of coating limited to 30 cm by 30 cm. The measurement of protection against different threats was conducted one by one, which might not reflect the real complex attack that the protective clothing suffered from. The comfort assessed was conducted on the fabrics rather than clothing, thus the understanding of the comfort after coating might be limited. Only polyurethane and silicone rubber membrane were chosen as the bottom layer of the coating, there might be other durable membranes that can be considered. For the functionalisation purpose, only PDMS and TMS together with fluoro-polymers were used for the creation of a cross-linked network.

8.3 Recommendation for future research work

During this research, a number of suggestions for proposed further work were identified.

1. The pad-knife-cure method is good for laboratory and industrial scales. However, the results of coating may vary when the production is scaled up. It is worthwhile to further develop this method in an industrial scale.
2. Deploying bottom layer membrane with uniform thickness and without affecting the breathability of the porous fibrous structure can be explored. Advanced fabrication techniques, such as electrospinning and electrospraying, could be adopted to overcome the issues from thickness, weight and comfort.
3. Cotton and polycotton fabrics were used in this research. The addition of repellent layers always comprised the moisture management properties of the cotton fabrics. Blended fabrics with cotton and poplin or wool, could probably maintain the thermophysiological comfort properties better without compromising the protection.
4. With a huge application potential in the chemical, biological, radiation and nuclear defence (CBRN), the protection side of this research work can be further extended to firefighting and biological, radiation and nuclear protection areas. Research into the antibacterial protection could be promising in developing protective gears against viral infection or biological pathogens/agents.

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10 APPENDICES

1 BLISTER /VESICANT AGENTS

Common name and designation	**Sulphur Mustard (HD)**	**Nitrogen Mustard**			**Lewisite (L)**
		HN_1	HN_2	HN_3	
Chemical formula	$C_4H_8Cl_2S$	$C_6H_{13}Cl_2N$	$C_5H_{11}Cl_2N$	$C_6H_{12}Cl_3N$	$C_2H_2AsCl_3$
Physical state at 20°C	Liquid	Liquid	Liquid	Liquid	Liquid
Volatility[mg/m^3]	906 at 25°C	2230 at 25°C	3490 at 25°C	120 at 25°C	3860 at 25°C
Persistency	Persistent	Persistent	Persistent	Persistent	Persistent
Stimulants	Methyl salicylate	-	-	Di methyl acetamide	Phenylarsine oxide
Effects	Skin, eyes and lungs	Affect the skin, eyes, respiratory tract and gastrointestinal tract. Like SM's, systemic absorption can lead to bone marrow suppression and central nervous system effects			Some features of arsenic toxicity can also develop
Protection	Protective masks & gas filters. Protective suits and decomintation wipes	Protective masks and gas filters. ($HN_1$and HN_2 are not used in the war zone		Protective suits, masks and gas filters	No Protective Suits are applicable in special situation
Penetration	It can easily penetrate ordinary clothing in vapour form	It can easily penetrate ordinary clothing in vapour form			It can easily penetrate ordinary clothing and even rubber

2 NERVE AGENTS

Common name and designation	**Tabun (GA)**	**Sarin (GB)**	**Soman (GD)**	**Cyclosarin (GE)**	**Vx**
Chemical formula	$C_5H_{11}N_2O_2P$	$C_4H_{10}FO_2P$	$C_7H_{16}FO_2P$	$C_7H_{14}FO_2P$	$C_{11}H_{26}NO_2PS$
Physical state at 20°C	Liquid	Liquid	Liquid	Liquid	Liquid
Volatility [mg/m^3]	497at 25°C	1.8x104 at 25°C	4x103 at25°C	898 at 25°C	10 at 25°C
Persistency	Non-persistent	Non-persistent	Non-persistent	Non-persistent	Persistent
Stimulants	di- ethyl ethylphosphonate (DEEP)	Diphenyl chlorophosph-ite (DPCP)	triethylphospha-te (TEP),	dimethyl methylphosph-onate (DMMP)	Amiton
Effects	Affect eyes, lungs, skin and nervous system. Blood prevent oxygen reaching body tissues	Affect eyes, lungs, skin and nervous system.	Affect eyes, lungs, skin and nervous system. Blood prevent oxygen reaching body tissues	Blood prevent oxygen reaching body tissues	Affect eyes, lungs, skin and nervous system. Blood prevent oxygen reaching body tissues
Protection	Protective masks and gas filters. Protective suits and decontamination wipes for skin irritants				
Penetration	Skin			Skin and inhaled in respiratory tract	Skin

3 CHOKING AGENTS

Common name designation	**Chlorine CL**	**Phosgene CG**	**Diphosgene DP**
Chemical formula	Cl_2	$COCl_2$	$C_2Cl_4O_2$
Physical state at 20°C	Gas	Gas	liquid
Volatility [mg/m^3]	$2.19\text{x}10^7$ at 25°C	$7.46\text{x}10^6$ at 25°C	$4.8\text{x}10^4$ at 20°C
Persistency	Non-persistent	Non-persistent	Non-persistent
Effects	Immediately after exposure patients complains of chest tightness, burning sensation in the nose, throat and eyes, redness and blisters on the skin like first bite.	Breathlessness and acute lung injury.	Effects on nose, throat and especially lungs
Protection	Protective suits.	Protective suits and protective masks.	Protective masks and gas filters. Protective ware suits
Penetration	Skin	Chloropicrin penetrates. Gas mask filters causing vomiting	Skin

4 ASPHYXIANTS/ BLOOD AGENTS

Common name designation	**Hydrogen cyanide AC**	**Cyanogen Chloride CK**	**Arsine SA (low toxicity)**
Chemical formula	HCN	CNCl	AsH_3
Physical state at 20°C	Liquids	Gas	Gas
Volatility [mg/m^3]	$1.1x10^6$	$2.6x10^6$	$31x10^6$
Persistency	Non-persistent	Non-persistent	Non-persistent
Effects	Chemical asphyxiates like cyanides interfere with oxygen transport at cellular level. Causing tissue hypoxia, anaerobic metabolism and lactic acidosis.	Causes breathlessness, headache, dizziness, anxiety, palpitations, mydriasis, blurring of Vision, nausea and drowsiness.	Inhaled arsine gas causes rapid destruction of red blood cells leading to hypoxia and renal failure.
Protection	Protective masks and gas filters. Protective suits.	Protective masks and gas filters. Protective suits	Protective masks and gas filters. Or Properly protected personnel should remove the victim from continued exposure to arsine.
Penetration	Skin	Skin	Skin

5 BEHAVIOUR AGENTS/VOMITING AGENTS

Common name designation	**Adamsite (DM)**	**Diphenylcyanoarsin (DA)**	**Diphenylchlore (DC)**
Chemical formula	$C_{12}H_9AsClN$	$C_{12}H_{10}AsCl$	$C_{13}H_{10}AsN$
Physical state at 20°C	Solid	Solid	Solid
Volatility [mg/m^3]	$26x10^3 – 120x10^3$ at 20°C	48 at 45°C	2.8 at 20°C
Persistency	Aerosol form: short, solid state: long		
Effects	Central nervous system, Eye, heart, respiratory system, skin, gastrointestinal tract, and urinary bladder.	central nervous system	Central nervous system, Eye, heart, respiratory system, skin, gastrointestinal tract, and urinary bladder.
Protection	Protective masks and gas filters. Protective suits.	Protective masks and gas filters. Protective suits.	Protective masks and gas filters. Protective suits.
Penetration	Skin	Skin	Skin