APPLICATION OF NANOCLAY ON POLYESTER FABRICS AS A BIO-INSPIRED APPROACH TO IMPROVE MOISTURE MANAGEMENT

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Degree of Master of Philosophy

Department of Chemical and Process Engineering

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Declaration of the candidate & supervisors

I declare that this is my own work and this thesis does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

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Abstract

Application of nanoclay on polyester fabrics as a bio-inspired approach to improve moisture management

Bio-inspired and biomimetic surface modifications are identified as one of the fascinating areas of research. In this study, nature's way of cooling elephants' body temperature using mud bathing was mimicked to create moisture management in polyester fabric. For that, bentonite nanoclay (BNC) was covalently grafted on polyester fabric using (3-aminopropyl) triethoxysilane (APTES) as a coupling agent. The novel modification method was proved qualitatively and quantitatively using characterization techniques such as X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR), X-ray diffraction (XRD), Scanning electron microscope (SEM), Transmission electron microscope (TEM), X-ray fluorescence (XRF) and Thermo gravimetric analysis (TGA). Moisture management tests, and physical and mechanical properties of modified polyester fabric were used to analyse the accomplishment of the modification. Hydroxyl groups on edges of BNC played a vital role in grafting with APTES. Primary amine group in APTES reacted with ester groups in polyester fibres, while silanols reacted with BNC. XRD analysis confirmed grafting of APTES on the surface of BNC without intercalation. XPS and FTIR spectroscopies confirmed the new secondary amide bond formation, while surface morphology was observed from SEM images. The significant enhancement in wettability, absorptive capacity, drying rate and wicking length proved moisture management property of polyester fabric. This fabric coating strongly withstood more than 10 cycles of laundry and against 5000 abrasion cycles. Physical and mechanical properties of modified fabrics remained unchanged, while tensile strength and elongation showed a slight improvement due to fibre preserving aminolysis reaction between APTES and ester groups in polyester fabrics. It is expected that this bio-inspired BNC modified polyester fabric may break the barrier of using polyester in various hydrophilic textile applications.

Keywords: Bentonite nanoclay, Covalent modification, Polyester, Biomimetic, Moisture management.

Dedication

To all my professors and doctors for the extensive knowledge you share with students like me. We are forever grateful to you for your unselfish guidance and especially for increasing our fascination for nanotechnology.

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Thank you all, whole heartedly.

Table of contents

List of figures

List of tables

List of abbreviations

Abbreviation	Description
AATCC	American Association of Textile Chemists and Colorists
APTES	(3-aminopropyl) triethoxysilane
ASTM	American Society for Testing and Materials
BNC	Bentonite Nano Clay
DTG	Derivative Thermo Gravimetric
EDX	Energy Dispersive X-ray spectroscopy
FTIR	Fourier-Transform Infrared
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IR	Infar Red
NRC	National Research Council
SEM	Scanning Electron Microscope
SLINTEC	Sri Lanka Institute of Nanotechnology
TEM	Transmission Electron Microscope
TGA	Thermo Gravimetric Analysis
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

List of appendices

xvii

1. INTRODUCTION

1.1 Background

Polyester is a man-made fabric, which has a greater demand in the clothing industry due to its characteristics such as improved wrinkle resistance, durability and high colour retention. However, these synthetic fabrics inherit undesirable properties to the wearer, such as low moisture gain, high flammability, and also the fibres have a tendency to accumulate static electricity. Thus, it has been identified the requirement for surface modifications of polyester to improve hydrophilicity, thermal properties, and permeability. There have been numerous research papers and patents published in this area and a considerable amount of research work is happening to improve the properties of polyester fabrics towards giving a comfortable fabric to the wearer. Recent studies are mainly focused on applying nanomaterials on polyester fabrics during manufacturing and finishing processes [1]. In textile finishing, nanoclay as a textile coating has gained much attention currently in the literature to bring new changes, such as flame retardant property [2]. Clay is known to have a very good cooling and detoxification effect [3].

In this study, hydrophilic bentonite nanoclay (BNC) was coated on polyester fabrics with the intension of increasing hydrophilic properties of the fabric. Thus, a comfortable naturally detoxicated fabric was achieved. Finally, physical and mechanical properties of BNC grafted APTES modified polyester fabric were evaluated, with the intension of identifying a simple, yet durable and economical approach to apply BNC on polyester fabrics with minimum alterations to fabric's physical and mechanical properties.

A National Research Council (NRC) grant (grant no. 16-101) was received to pursue this research. The research was carried out at Sri Lanka Institute of Nanotechnology (Pvt) Ltd (SLINTEC), with the availability of characterization equipment such as Scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier-transform

infrared (FTIR) and Thermo gravimetric analysis (TGA). Evaluation of fabric mechanical properties were carried out at Department of Textile and Clothing Technology, Faculty of Engineering, University of Moratuwa.

1.2 Statement of the problem

Polyester fabrics have become very successful in the fashion industry due to their outstanding properties such as high strength, resistance to abrasion, shrinking, wrinkling and ability to withstand many of the chemicals and environment conditions. However, the hydrophobic surface structure due to the lack of polar groups on the surface brings difficulties in textile processing and full utilization of polyesters in the apparel market. Apparel consumers have complained that synthetic fabrics like polyester give an unpleasant skin contact and thermal sensation, lack of moisture absorbency and creation of static related problems, which are results of the low surface energy and poor moisture regain of polyester.

Surface modification methods play an important role in increasing surface energy of polyester fabric, which in return increase moisture regain. Currently available surface modification methods, such as chemical modifications and processing modifications, lack effectiveness and sustainability in the market due to toxicity, low durability and high cost in application [4-7]. Strong alkaline treatments at high temperature are the most utilized way to improve the hydrophilicity of synthetic fabrics [8]. However, this process requires high consumption of chemicals and energy, and if not controlled properly, a significant strength and weight loss of polyester fibres can occur due to peeling mechanism by alkaline attack. Fluorinated derivatives are also used widely in increasing hydrophilicity of polyester. However, these methods lack wash fastness property and decrease fabric softness [9]. Hence, these methods require the use of an additional softener.

Every time after a fabric surface modification, for the inevitable desirable fabric property losses, an additional fabric finishing such as softener is needed. This results in increasing costs. Therefore, when developing fabric surface modifications, the

negative effect on fabric's desirable properties needs to be minimized. Therefore, an understanding of physical and mechanical properties of fabrics subsequent to any new finishing treatment is crucial for efficient utilization of the treated fabric in clothing, household, medical or any other textile application [10].

Although surface modification of polyester to improve hydrophilicity has been reported across literature, due to the problems mentioned above, still there is a requirement to develop an industrially sustainable and consumer benign moisture management method for polyester fabrics.

1.3   Purpose of the study

Polyester is a man-made fabric, which has a greater demand in the clothing industry due to its characteristics such as improved strength, wrinkle resistance, washability, durability and high colour retention. However, these synthetic fabrics inherit some undesirable properties to the wearer, such as low moisture regain and high flammability. Polyester fibres have a tendency to accumulate static electricity, which is problematic in garment cutting and sewing. Polyester has a 0.4% moisture regain, whereas it is 7.0% in cotton (American Society for Testing and Materials (ASTM) standards, 2004), since it is made up of a hydrophobic polymer, polyethylene terephthalate. This hydrophobic nature of polyester results in a relatively low level of comfort to the wearer, as moisture is neither absorbed nor drawn away from the skin. This accumulated moisture along with the body warmth can provide an ideal proliferation ground for microbes, which lead to unpleasant odours, staining, fabric deterioration, and even skin allergies and skin infection [10, 11]. This has restricted the use of polyester in many textile applications such as sportswear, underwear and bedding.

Moisture management is one of the key performance criteria in today's apparel industry. Hence, creating hydrophilic polyester fabrics to meet market needs has been explored via chemical modifications and processing routes [12, 13]. Most of the times the chemical modifications lead to increased costs for the fabric manufacturers.

Further, most surface level chemical modifications exhibit poor wash fastness property and lesser dye uptake [8, 14]. Moreover, processing routes cause to decrease mechanical and physical properties of the original fabrics [13]. Therefore, researches are being undertaken on new ways to achieve more durable hydrophilic polyester without impacting the mechanical, physical and comfortable properties of the original polyester fabrics.

With the advent of nanotechnology, manipulating materials at nanoscale (1 nm – 100 nm), a new era has emerged in creating new functional textile materials. The nanotechnology research in textile industry mainly centres around creating unique properties in everyday fabrics, such as self-cleaning, water and oil repellency, stain proof, antibacterial, UV protective, antistatic or hydrophilic properties in synthetic textiles [1]. Nanofinishing, nanocoatings, nanofibres and nanocomposites are being used to increase moisture regain of polyester fabrics [1, 15, 16]. The new range of hydrophilic nanofinishes, 'Cotton Touch' and 'Coolest Comfort' commercialized by Nano Tex, USA, makes synthetic fabrics look and feel like cotton (www.nano-tex.com). Currently, the high-tech outdoor apparel market is eager to obtain and pay for fabric innovations. However, many traditional textile and garment industries are reluctant to add more cost to their production in an already competitive market. Hence, when adding value to textiles by enhancing their properties, the cost effectiveness of the introduced new methods needs to be considered for these value added products to sustain in an already competitive market.

Nature always provides sustainable, cost-effective, multi-purpose and flexible alternatives for various problems of the eco system. Animals, in this regard, use various natural resources and techniques to adapt to different environmental conditions. One such technique is 'mud-bathing' used by elephants in response to high temperature in order to reduce the heat load and to get rid of flies [3, 17]. Generally, the fine soils or peat are preferred as substrates for bathing [18]. By mimicking the nature's way of cooling elephant's body temperature using the moisture management properties of mud, BNC was identified as an ideal sustainable solution to develop a polyester fabric with improved comfortable properties.

BNC in textile coating is one of the modern technologies, which brings revolutionary changes into functionality of textiles [19]. BNC is commonly any group of important hydrous aluminium silicates with a layered structure, and its thickness is in the nanometre scale. Particle size, surface area and aspect ratio are highly important characteristics desired in BNC applications. The length and breadth of these particles can range from 1.5 μm to a few tenths of a micron [20, 21]. The thickness of BNC is exceptionally smaller relative to its length. Therefore, an extremely high average aspect ratio (length to diameter ratio) of 200 to 500 is possible. A small amount of BNC exhibits a high surface area; i.e. a BNC product is known with a surface area in excess of 750 m^2/g [20]. Therefore, small addition of BNC can greatly enhance the desirable properties of fabrics.

According to the literature, BNC could not be covalently attached onto the surface of polyester fabrics using a simple one step process. In this study, BNC are functionalized with (3-aminopropyl) triethoxysilane (APTES). APTES contains amine groups, which react with ester bonds on the surface of the fabric to form covalent bonds.

1.4   Objectives

There are four main objectives of this study.

A. To find a suitable surface modification method to apply BNC onto polyester.
B. To develop a method to treat BNC on polyester, considering moisture management functionality.
C. To investigate the effects of the selected method on morphological, durable, physical and mechanical properties of polyester fabrics.
D. To understand the surface modification as well as the other possible interaction created between modified BNC and polyester fabric.

1.5   Significance of the study

Sri Lankan apparel industry was at its best in the export business last few decades, with the low labour cost and production with high quality. However, currently, competitors such as Bangladesh, India and China have also achieved these competitive advantages gradually. Therefore, Sri Lanka should start looking for other avenues to win this intense competition in garment exports. In order to get more profits as competition intensifies in conventional garment manufacturing, there needs to be substantial value addition to textiles. To popularize less expensive polyester clothes in the emerging Asian tropical climatic markets, the attention needs to be on making wearer more comfortable by introducing proper moisture management to the fabric.

This study introduces simple, cost effective, sustainable and biocompatible method to improve moisture management property of polyester fabrics. Silane modified BNC is stable over a wide range of storage and use conditions. Small addition of silanized BNC enhances hydrophilicity of polyester, while remaining its original property unchanged. High energy and chemical consumption is minimized as an answer to existing surface modification methods.

It is well evident that silanization has biological applications such as immobilization of biomolecules, particularly proteins, and also clay is being involved in numerous ways of our lives. Hence, this methodology is biocompatible, while most of the other types of functionalization of BNC on fabrics are not sustainable and sometimes threatening to our lives.

1.6   Chapter framework

This thesis consists of five chapters in total, describing the research study in detail. Having introduced the thesis and the research here in this introductory chapter, Chapter 2 identifies and appraises the literature in understanding textiles and their moisture management, and different types of clay, which forms the base of this

study. This chapter further identifies existing functionalization of textiles with both moisture management property and clay, while recognizing characterization of moisture management fabrics and their physical and mechanical properties.

Chapter 3 is dedicated to describe the research methodology in detail, whereas Chapter 4 of the thesis discusses the corresponding research results. These two chapters address the different tests carried out in relation to selection and characterization of clay and coupling agent, creation of BNC grafted APTES modified polyester, characterization, wash fastness properties, and moisture management properties of the BNC grafted APTES modified polyester. These are followed by the testing of mechanical and physical properties of the fabric created. Chapter 5 presents the conclusions and recommendations of the research, derived from results and discussion in Chapter 4.

2.   LITERATURE REVIEW

2.1   Introduction

This chapter reviews published literature related to basics of polyester fabric textiles, desirable and undesirable properties of polyester fabrics, and poor moisture management property of polyester fabrics. Then, existing modification to improve moisture management property of polyester fabrics and their drawbacks are explored. Further, clay as a material to improve moisture management property of polyester fabrics is reviewed.

2.2   Understanding of textiles

This section seeks to explore evolution of textile fibres, classification of textile fibres and synthetic fabrics.

2.2.1   The textile fibres

Textiles comprise of fibres or filaments which are made of natural material such as silk, wool, cotton and linen, and man-made materials such as polyester, nylon and rayon. The name for textile was derived from Latin term "texere", meaning "to weave" [22]. Thus, the fibres or filaments are woven or knitted in order to make fabrics. The tool originally used for weaving was the loom in ancient Egypt around 3400 B.C. Then, textiles were being produced to meet market requirements. In China, silk was spun and woven into silk fabrics, while the European population wore clothes in wool, linen and leather from 2600 B.C. onwards [23]. Upon invention of the mechanically driven loom, the production of textiles was done in mass scale at lower cost in order to satisfy the ever growing demand for the textiles. Owing to industrial revolution in 18th and 19th centuries, fibre processing machineries were invented. As a result, nylon fibres were made at the end of the 19th

century. Then, the discovery of polyester, acrylic and other synthetic fibres were taken place from 1940 to 1950 [22].

New blends of fibres were produced by mixing natural and synthetic fibres in 1952. Upon production of the fibre blends, a novel concept for clothing was popular among the consumers, which was cold as "wash and wear" [24]. This term was used especially to draw more consumers for this new fibre blend. These new fibre blends had desirable properties to the wearer such as wrinkle free, so it could be wearable by wash only and its strength made it an easy care product [25]. The polyester fibre was a turning point in the textile industry. Since then, new shape retaining knitwear with higher durability came into actuality. The garments made by polyester fabrics gained popularity in 1970's. With the new developments and discoveries, the industry of manufactured fibres is diversified.

2.2.2   Classification of textile fibres

To distinguish and understand the properties of fibres, they are majorly divided into two classes, namely natural and man-made (Figure 2.1). The main two classes are further divided into sub-classes. Natural fibres fall into three sections, namely animal, vegetable and mineral, while the man-made fibres are divided into natural polymers, synthetic polymers and non-polymeric [26]. The fibres that are derived from plants are called vegetable fibres or cellulosic fibres, in which carbon, hydrogen and oxygen elements are present. They inherent good properties like high absorption capacity, low resilience, high density, resistant to high temperature, and act as good conductors of heat [27]. Wool and silk are common examples of animal fibres, which consist of protein molecules. Mineral fibres are mainly utilized for engineering purposes in fire proof and acid proof fabrics [28]. Man-made fibres refer to all fibres or filaments manufactured by man from chemical elements or compounds, as distinct from those which occur naturally. These fibres have high strength and low moisture absorption characteristics [29]. Examples of man-made fibres are nylon, polyester, terylene, orlon, dynel, rayon, etc. Depending on raw material chosen for making of the fibres, they are classified as natural polymer, synthetic polymer and non-

polymeric. Especially, the synthetic fibres are produced from polymers which are chemically synthesised.

2.2.3 Elements of fabric structures

An assembly of relatively small cross section and long filaments or fibres with or without twist is defined as a yarn [30]. These yarns are transferred to fabric by knitting, weaving and various non-woven processes. According to the way the yarns of fabric interlace each other, they can generate different structures. An interlacing where the filling threads are passed alternatively over and under the warp threads is called as a plain weave [31]. It is the simplest of all weaves. Woven fabrics comprise of warp and weft yarns, which are interlaced with each other. The yarns that run parallel to the selvedge of the fabric are called as warp, and the yarns running perpendicular to selvedge of the fabric are called weft. When considering the methods of manufacturing textile structures, weaving takes a major place while knitting has its second place. Knitting necessitates a relatively fine, smooth, strong yarn with good elastic recovery properties [30]. A nonwoven is another textile structure produced by interlocking or bonding of staple and continuous fibres, using thermal, chemical, mechanical or solvent treatments. Manufacturing of non-woven is a continuous process, and also it is an advantage. In this process, manufacturing is directly started from the raw material and ends up with final fabric. Up to now, all discussed fabric types are single plane (2-D) structures. However, more complicated fabric structures like fabric in 3-D structures can be prepared by knitting, weaving, non-woven and braiding [32]. Hence, this diversified fabric manufacturing allows more flexibility and diverse applications to meet exponentially growing demand in the market.

CLASSIFICATION OF TEXTILE FIBRES

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                        CLASSIFICATION OF TEXTILE FIBRES
                                        |
            ┌───────────────────────────┴───────────────────────────┐
         Natural                                                Man-Made
            |                                                        |
  ┌─────────┼──────────────┐                        ┌───────────────┼──────────┐
Animal           Vegetable        Mineral      Natural         Synthetic    Non-
  |                  |               |          Polymer         Polymer    Polymeric
  |          ┌────┬──┴──┬────┐    Asbestos         |               |          |
Staple  Filaments Seed Bast Leaf Fruit     ┌───┬───┼────┬────┐                Metal
  |          |      |    |    |    |      Protein Rayon Cellulose Miscellaneous Threads
  |        Silk  Cotton Flax Manila Coir  (Ardil, (Viscose, Esters  Alginate,
┌─┴───┐         Kapok  Jute  Sisal        Lanital, Cupram- (Cellulose Rubber
Wool Hairs             Hemp  Raffia        Vicara, monium) Acetate)  Threads,
      |                Ramie Phormium      Fibrolane,                 Silica, etc.
     Goat              Nettle Tenax        Aralac,
     Camel             Hibiscus            Tiolan,
     Hare                                  etc.)
     Rabbit
     Horse
     Cow
```

Organic Origin   Inorganic Origin

Inorganic Origin — Glass (Fibreglass)

Organic Origin:

- Polyesters (Terylene Dacron)
- Polyamides — Nylon 6 (Perlon), Nylon 66, Nylon 11 (Rilsan)
- Polyurethanes (Perlon U)
- Vinyl Derivatives

Vinyl Derivatives:

- Polymerised Hydrocarbons — Polyethylene (Polythene, Alkathene), Polystyrene (Polyfibre, Algil)
- Chlorine Substituted (Vinyons), Vinylidene Chloride (Saran, Velon), Rubber (Substituted Hydrocarbons), Polyvinyl Chloride (Rhovyl, Thermovyl, Isovyl, Fibravyl PeCe, PCU)
- Acrylics (Orlon, Acrilan, Dynel, Redon)
- Polyalcohols (Vinylon, Kanebryan)

Figure 2.1: Classification of textile fibres [26]

11

2.2.4 Synthetic fabrics

Synthetic fabrics are produced using synthetic fibres (Table 2.1). Polymerization is involved in making these synthetic fibres. Polymerization is a process that involves the linking of monomers into polymers under necessary conditions [33]. These fibres offer a range of advantages, such as durability, lightweight nature, wrinkle resistance, and high lustre among others. When compared with natural fibres, man-made fibres are a more affordable alternative to ever growing needs such as clothing, automotive, home furnishing and other industries. Therefore, the current statistics show that the global synthetic fibre market is expected to grow at 7.25% over the forecast period from 2018 to 2023. Further, it has also shown USD 95,316.8 million revenue being generated by the market in 2017 and is expected to grow to generate a revenue of USD 144,279.9 million by the end of 2023 [34].

Synthetic fibres are highly popular in use for sports garments, home furnishing and as upholstery fabric, which has been identified as a key market driver over the assessment period. Further, advancement in production technology of synthetic fibres and new modification concepts are expected to strengthen the market growth over the forecast period. Lightweight and durability of synthetic fibre materials are in high demand, owing to their ability to provide more benefits. Synthetic fibres have gained more consumer attraction due to the strength and cost-effectiveness of these fibres [29, 33]. Moreover, other positive properties such as corrosion resistance and design flexibility are expected to expand the global synthetic fibre market. All man-made fibres differ in their unique compositions and physical properties. The U.S. Federal Trade Commission has established generic names for man-made fibres, including polyester, nylon, acetate, acrylic, rayon, spandex, lyocell, modacrylic and polypropylene [35]. However, this implies that all fibres under one generic name are not exactly the same and there are slight changes in polymer structures.

Table 2.1: Synthetic fibre constitution [33]

Fibre type	Chemical formula of principal repeat unit
Polyamide:	
nylon 6,6	$-NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO-$
nylon-6	$-NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO-$
Polyester:	
polyethylene terephthalate	$-O \cdot CO \langle \bigcirc \rangle CO \cdot O \cdot CH_2 \cdot CH_2-$
Acrylic:	
polyacrylonitrile	$-CH_2 \cdot CH-$ $\quad\quad\ \ \|$ $\quad\quad\ C \equiv N$
Polyolefin:	
polyethytlene	$-CH_2-$
polypropylene	$-CH_2 - CH-$ $\quad\quad\quad \|$ $\quad\quad\quad CH_3$
Polylactic acid	$-CO \cdot CH(CH_3) \cdot O-$
Other addition-polymer fibres:	
polyvinyl cholride	$-CH_2 \cdot CHCl-$
polyvinyl alcohol	$-CH_2 \cdot CH-$ $\quad\quad\ \ \|$ $\quad\quad\ OH$
other vinyl monomers	$-CH_2 \cdot CH-$ $\quad\quad\ \ \|$ $\quad\quad\ R$
vinylidene monomers	$-CH_2 \cdot CR_2-$

2.3   Polyester fabrics

International Bureau for Standardization of Man-made Fibres (BISFA) defines polyesters as fibres manufactured using any long-chain polymer comprising of no less than 85% by weight of an ester of a substituted aromatic carboxylic acid comprising, but not limited to, substituted terephthalate units [36, 37]. This suggests that there are different polymer structures under the polyester generic name. The most common molecular structure or repeating unit of polyester is depicted in Figure 2.2. Polyester chains, unlike cellulosic fibres, do not form hydrogen bonds between molecules, but are held together by the dipole-dipole interactions. Polyester is recognized as a tough and strong fibre with a significant tensile strength and resistance to elongation [38]. Degree of crystallinity of polyester fibres differs according to the application. For instance, clothing and household fabrics are around 65% amorphous and 35% crystalline, whereas less amorphous and more crystalline

13

are suitable for technical applications. Higher crystallinity provides not only a stronger, but also a stiffer polymer [39].
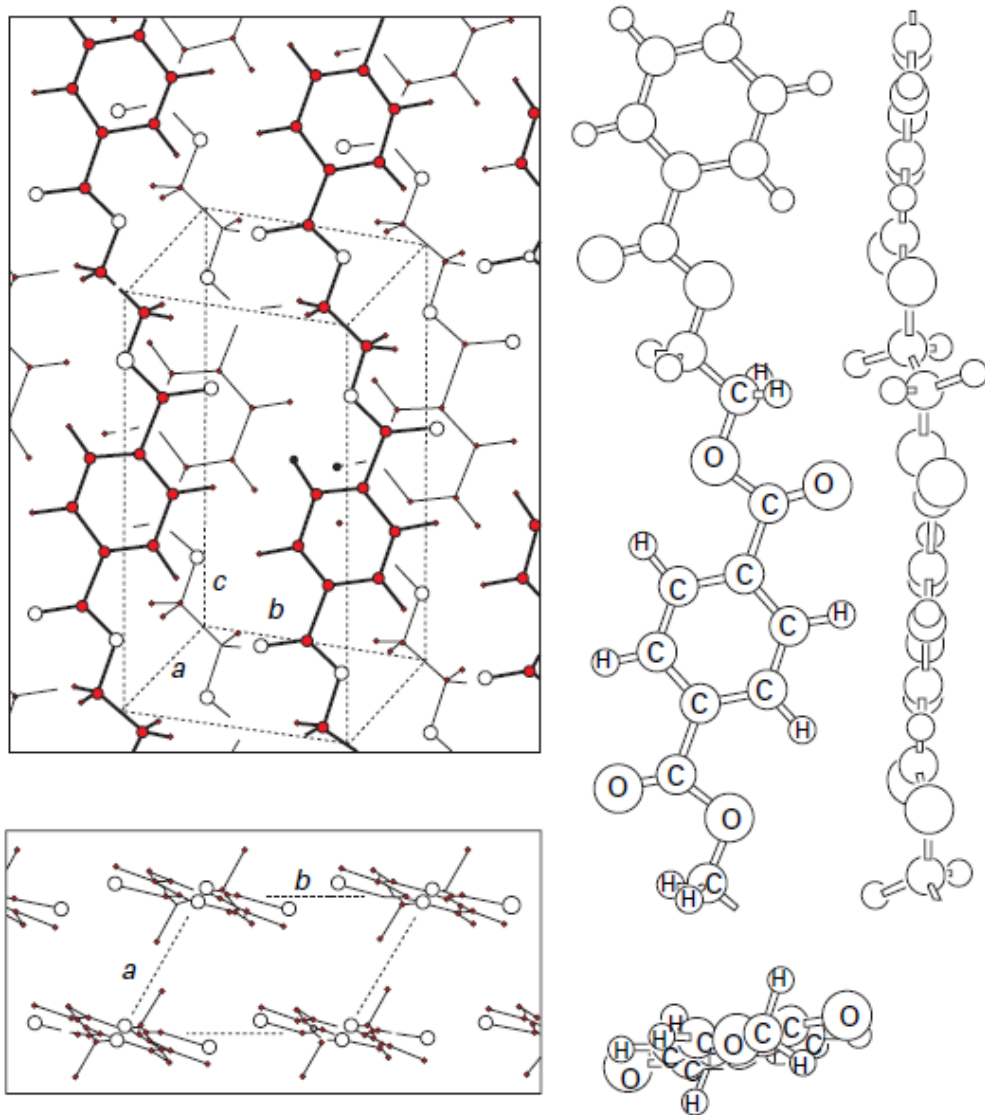
Figure 2.2: Atomic structure of polyester fibre [37]

2.3.1 Desirable properties of polyester fabrics

Under the polyester generic name, Poly(ethylene terephthalate) is the main member of polymer, which is the widely used fabric in the textile industries. Polyester fabrics exhibit desirable properties, such as improved wrinkle resistance, durability, dimensional stability, washability, high colour retention, high tensile strength, and

resistance to many different chemical and environmental conditions [39]. These incredible qualities make the polyester fabric an outstanding material not only for garments, but also for domestic, medical, technical and automotive textiles [40]. Statistics show that sharing of polyester in the total textile production is about 42% and has begun to grab market share over cotton [40]. This is due to the advantages mentioned above, along with readily availability and low cost of the raw materials.

2.3.2   Undesirable properties of polyester fabrics

Unfortunately, unlike most of the synthetic polymers, polyester does not show wetting and hydrophilic properties, owing to its characteristically low surface free energy. As stated earlier, polyester does not contain water affinity groups, such as – NH_2, –COOH and –OH groups. Hence, this dormant nature of polyester fabrics results in innate hydrophobicity and limited reactivity. Low moisture regain, low sweat absorbency and thermal irritation have been created by the low surface free energy and resulting poor adhesion to other materials [41]. Polyester has a 0.4% moisture regain, whereas it is 7.0% in cotton (ASTM standards, 2004), since it is made up of a hydrophobic polymer, polyethylene terephthalate [42, 43]. This hydrophobic nature of polyester results in a relatively low level of comfort to the wearer, as moisture is neither absorbed nor drawn away from the skin. This accumulated moisture along with the body warmth can provide an ideal proliferation ground for microbes, which leads to unpleasant odours, staining, fabric deterioration, and even skin allergies and skin infection [44-46]. Polyester fibres have a tendency to accumulate static electricity, which is problematic in garment cutting and sewing. This has restricted the use of polyester in many textile applications such as sportswear, underwear and bedding. Thus, it has been identified the requirement of surface modifications to polyester to improve wettability, thermal sensation and permeability.

2.4   Moisture management of polyester fabrics

This section seeks to map existing literature on moisture management of polyester fabrics and their drawbacks.

2.4.1   Introduction to moisture management

In the modern world, consumers have too many choices when selecting a garment due to diversification of textile products. However, commonly consumers demand some properties in clothing when it comes to comfort wearing. Now-a-days, consumers are extra demanding on performances of clothing, particularly for leisure and sportswear. Therefore, more attention has been driven to develop improved garments in terms of comfortability [47]. Wear comfort of garment can be divided into four parameters in terms of comfortability such as thermo-physiological comfort, skin sensorial comfort, ergonomics wear comfort and psychological comfort [48]. The Human body thermoregulates in four modes, namely conduction, convection, radiation and evaporation. In these conditions, evaporation remains the only mode for heat loss. The heat loss is governed by the rate of sweat evaporation and relative humidity of the environment. Thermo-physiological comfort of a fabric depends on moisture management ability and breathability. Fabric makes a microclimate between the skin and the environment, and acts as a barrier for heat and water vapour transfer from the skin to the environment. Therefore, fabric should satisfy this heat and water vapour transfer without obstructing the evaporation of humidity resulted by perspiration, avoiding interference with body temperature regulation. Hence, all these mechanisms imply that moisture management is a key performance criterion of present apparel industry, deciding the level of comfort of the fabric. In order to cool the body, clothing should transport moisture to its outer surface and evaporate moisture quickly. Therefore, moisture management is defined as the controlled movement of liquid water (i.e. perspiration) and water vapour from the skin surface to the atmosphere across the fabric [49-52]. When fabric surface contacts with skin, it absorbs moisture and transfers it to the outer surface of fabric through wicking. In severe sweating conditions, rapid absorption of liquid by the

fabric is not sufficient and it needs transport of liquid to the outer surface of the fabric promptly to avoid the discomfort of the fabric sticking to the skin.

2.4.2   Moisture management of polyester fabrics

A wide variety of physical, chemical modifications and technologies have been used to improve poor moisture management of polyester fabrics. The most of modifications of textiles were reported using physical treatments such as corona discharge, plasma, laser and electron beam [53-57]. These methods were able to alter the fibre surface from lack of functional groups to hydrophilic functional groups. Further, plasma etching increases porosity of fibres. In contrast, chemical methods such as surface grafting, enzymatic modification and sol-gel technique were reported as attempts to improve wettability of polyester fabrics [58-61]. The introduction of functional groups, which have affinity to water, have been reported in many research works such as nitrogen-containing functionalities. This modification has been achieved via wet chemical reactions and incorporating amino groups, and this leads to alter the chemical nature of polyester fabric, allowing its surface to adapt to different applications. Using of chitosan in modifying the polyester fabric surface has been reported as a key probable approach in introducing amino groups. On the other hand, microfibers and silicon containing softeners have been used to enhance moisture management of polyester fabrics. Microfibers also influence the hydrophilic properties due to mechanisms of moisture transport in fabrics. Waterproof breathable fabrics and hydrophilic fabrics can be considered as some advances in the area of moisture management in textiles [62]. The application of softening agents was able to increase hydrophilicity of fabrics at molecular level. With the advent of technology, researchers and manufacturers were able to alter the shape of fibres in order to provide effective moisture transfer. Bean, trilobal and oval were some of the improved shapes for fibre structures [63]. These fibre shapes accelerate moisture transfer, providing micro channels and significant surface area.

2.4.3　Problems of existing modifications for polyester fabrics

In respect of surface modifications mentioned previously, their drawbacks need to be considered. Chemical modifications such as aminolysis inadvertently and alkaline hydrolysis involve polymer deterioration and degradation. Further, the surface level modifications such as layer-by-layer removal exhibit poor wash fastness property due to insufficient bonding with the fibres [64]. Moreover, physical modifications such as plasma treatment cause to decrease mechanical and physical properties of the original fabrics [53-56]. This layer-by-layer removal of the top surface of polyester fibres results in loss of fabric strength, and ultimately affecting the overall product performance adversely. These adverse effects reduce the range of fabric applications, especially in technical areas. Therefore, researches are being undertaken on new ways to achieve more durable hydrophilic polyester, without impacting the mechanical, physical and comfortable properties of the original polyester fabrics.

Furthermore, due to the generation of hazardous and corrosive chemical waste, these conventional modification methods can be considered as creating a greater negative impact to the environment [54, 56]. The new range of hydrophilic nanofinishes, 'Cotton Touch' and 'Coolest Comfort' commercialized by Nano Tex, USA, makes synthetic fabrics look and feel like cotton (www.nano-tex.com). Currently, the high-tech outdoor apparel market is eager to obtain and pay for fabric innovations. However, many traditional textile and garment industries are reluctant to add more cost to their production in an already competitive market. Hence, when adding value to textiles by enhancing their properties, the cost effectiveness of the introduced new methods needs to be considered for these value added products to sustain in an already competitive market. In contrast, it is vital for polyester fabric to undergo pre-treatment prior to adhesion improvement modification, due to the limited reactivity of polyester fabric surface. For instance, alkaline hydrolysis with sodium hydroxide is said to make polyester fabric more wettable due to hydroxyl and carboxylic groups. Therefore, considering all these negative effects as a challenge, it is important to look for alternative surface engineering methods, which cause less

environmental contamination and consume less energy during textile finishing processes.

2.5   Bio-inspired method to improve moisture management property

Wallowing is a natural behaviour of wild animals, where the body surface is coated with mud or a mud-like substance. Wild animals such as elephants, pigs, buffalo, hippos, zebras, etc. have a practice to mud bathe in response to high temperature, in order to reduce the heat load [3]. For instance, elephants cool their bodies by applying a thick layer of mud, which also helps them to keep the coolness for long periods of time and get rid of flies. The common perception is that pigs wallow mainly for cooling, sunburn protection and removal of ectoparasites. However, pigs lack functional sweat glands and wallowing in mud is an effective behavioural control mechanism in pigs to prevent hyperthermia. Animals may also dust bathe to get rid of ectoparasites as they rub their bodies against the soil particles or they may dust bathe as a skin care mechanism [17, 65]. The behavioural studies about wallowing wild boar show that wallowing is not only for thermoregulation, ectoparasite removal and protection from sunburn, but also for disinfection of wounds. Apart from that, especially birds practice dust bathing, which serves to remove dirt and excess oil from the feathers and to improve structures of feathers [66]. Moreover, fine soils such as sand or peat are preferred as substrates for dust baths. Hens are lying down and pulling loose substrate close to its body by rubbing itself on the substrate and then shaking its wings and body to toss the soil on its back and work it through the feathers. Asian elephants dust bathe by pinching soil with the side of their trunks and throwing it onto their body [17]. In contrast, Mud-bath was practiced in ancient Greece, and has been used in central Europe for the last 200 years, mainly for treating arthritis and gynaecological disorders. Mud-bathing gave impressive results by absorbing of its various substances into the body. Further, therapeutic clay packs have been used for internal body issues such as boosting the immune system, easing muscle tension and removing toxic bioaccumulation. Therefore, considering the benefits of mud mentioned above, it is wise to keep a layer of mud or clay as close to us as possible all day long. To suffice this, one can

only think of clothing as the closest commodity to the human body. By mimicking the nature's way of cooling elephant's body temperature using the moisture management properties of mud, clay was identified as an ideal sustainable solution to develop a polyester fabric with improved comfortable properties.

2.6   Understanding clay

This section seeks to explore the clay, varieties of clay and properties of bentonite clay in favour of moisture management.

2.6.1   Clay

Clay is a ubiquitous mineral in nature, which refers to a group of hydrous aluminosilicates [20, 67]. These minerals show a similar structural and chemical composition to the primary minerals on the earth's crust. Nevertheless, weathering made them differ in geometric arrangement of ions and atoms. Clay minerals exhibit a layered structure. The fundamental structural unit of clay is a SiO_4 tetrahedron. Its structure is depicted in Figure 2.3 (a). A sheet tetrahedral is an array of these tetrahedra connected in the same plane. It is shown in Figure 2.3 (b). An aluminium, magnesium or iron ion typically serves as the coordinating cation. Then, the cation is surrounded by six hydroxyl groups or oxygen atoms. The other building block of clay called octahedron is shown in Figure 2.3 (c). An octahedron is formed with the aid of coordinating cations such as aluminium, magnesium or iron. The interconnected several octahedra are called the octahedral sheet, and its structure is shown in Figure 2.3 (d). For instance, the molecular arrangement of gibbsite $A1(OH)_3$ and brucite $Mg(OH)_2$ are similar to that of octahedral sheets. Above mentioned structural arrangements are the primary templates for clay minerals. Nevertheless, the composition changes often owing to substitution of ions within the clay structure. This weathering facilitates the substitution of silicon, aluminium and magnesium ions with cations. Consequently, silicon ions (Si^{4+}) may be replaced by aluminium ions (Al^{3+}) in the centre of the tetrahedron. Moreover, cations such as iron ($Fe^{3+/2+}$) and zinc (Zn^{2+}) may replace aluminium (Al^{3+}) and magnesium (Mg^{2+}) ions

in the octahedra. Hence, this replacement of one structural cation with another of similar size is known as isomorphous substitution. The isomorphous substitutions occur for both positive and negative charges in clay minerals. Different clay minerals differ in the arrangement of sheets. Therefore, this leads to possess different chemical and physical properties for different clay minerals.
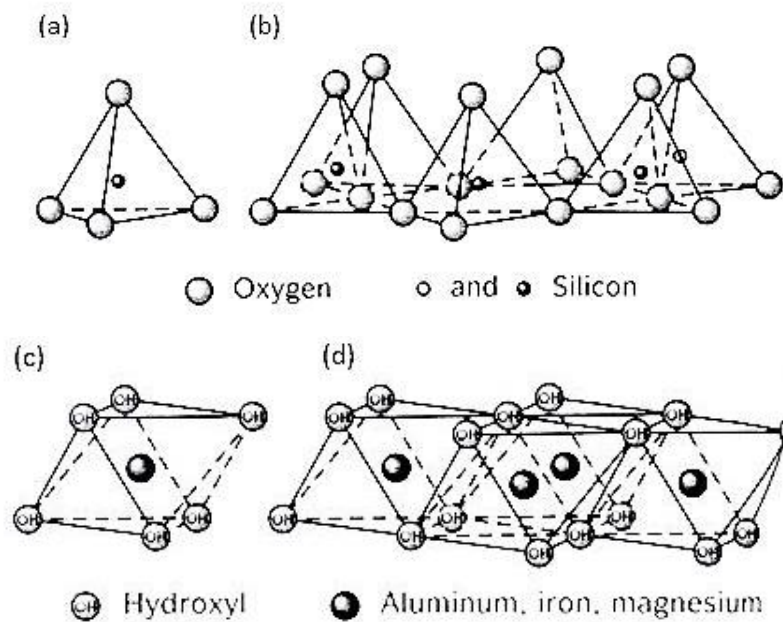
Figure 2.3: (a) A single structure of silica tetrahedron, (b) a sheet structure of silica tetrahedra arranged in a hexagonal network, (c) a single octahedral unit, and (d) a sheet structure of octahedral units [67]

2.6.2 Classification of clay

According to the arrangement and the number of tetrahedral and octahedral sheets, clay minerals are divided into 3 layer types. However, these are further classified into 5 groups, considering their net charge [20, 67].

1:1 clay mineral would have one tetrahedral and one octahedral sheet per clay layer (Figure 2.4). Kaolin is another name for this two-sheet mineral group and its general formula is $Al_2Si_2O_5(OH)_4$. Kaolinite is categorized under this clay mineral type. There

are van der Waals bonds between hydroxyls of the octahedral sheet and basal oxygens of the tetrahedral sheet, which keep the sheets together. Layers are held by hydrogen bonding, which restricts expansion and limits the active surface area. Kaolinite exhibits a poor cation adsorption due to lack of substitution for Si^{4+} and Al^{3+} ions.

The 2:1 layer minerals contain two tetrahedral sheets and one octahedral sheet, sandwiched between the two tetrahedral sheets. Smectite, mica and vermiculite groups represent these 2:1 type minerals. For instance, talc [$Mg_3Si_4O_{10}(OH)_2$] and pyrophyllite [$Al_2Si_4O_{10}(OH)_2$] are characteristic clay minerals for electrically neutral 2:1 type. The adjacent layers of these minerals are joined to each other through van der Waals bonds. Micas have a structure similar to pyrophyllite and talc, except for the fact that silicon (Si^{4+}) ion being substituted by aluminium (Al^{3+}) ion in every fourth tetrahedral. This results in an excess of one negative charge per formula. This negative charge is satisfied by potassium (K^+) that exists on interlayer sites between the 2:1 layers. Hence, potassium (K^+) forms a stronger bond between adjacent tetrahedral sheets, resulting in a limited expansion of the mineral.

Expandable 2:1 clay minerals (Figure 2.4) exhibit a layered structure similar to that of mica. However, owing to the presence of weakly bound polar organic molecules, cations or water in the interlayer region, layer charge and interlayer spacing differ widely. In general, a group of expandable dioctahedral 2:1 minerals are referred to as smectites. Montmorillonite, which has versatile applications, belongs to this 2:1 group and it has a negative charge due to octahedral isomorphous substitution of Mg^{2+} for Al^{3+}. Van der Waals bonds and attraction forces between cations in the layers and oxygen atoms in the clay structure hold together the 2:1 layers of smectites.
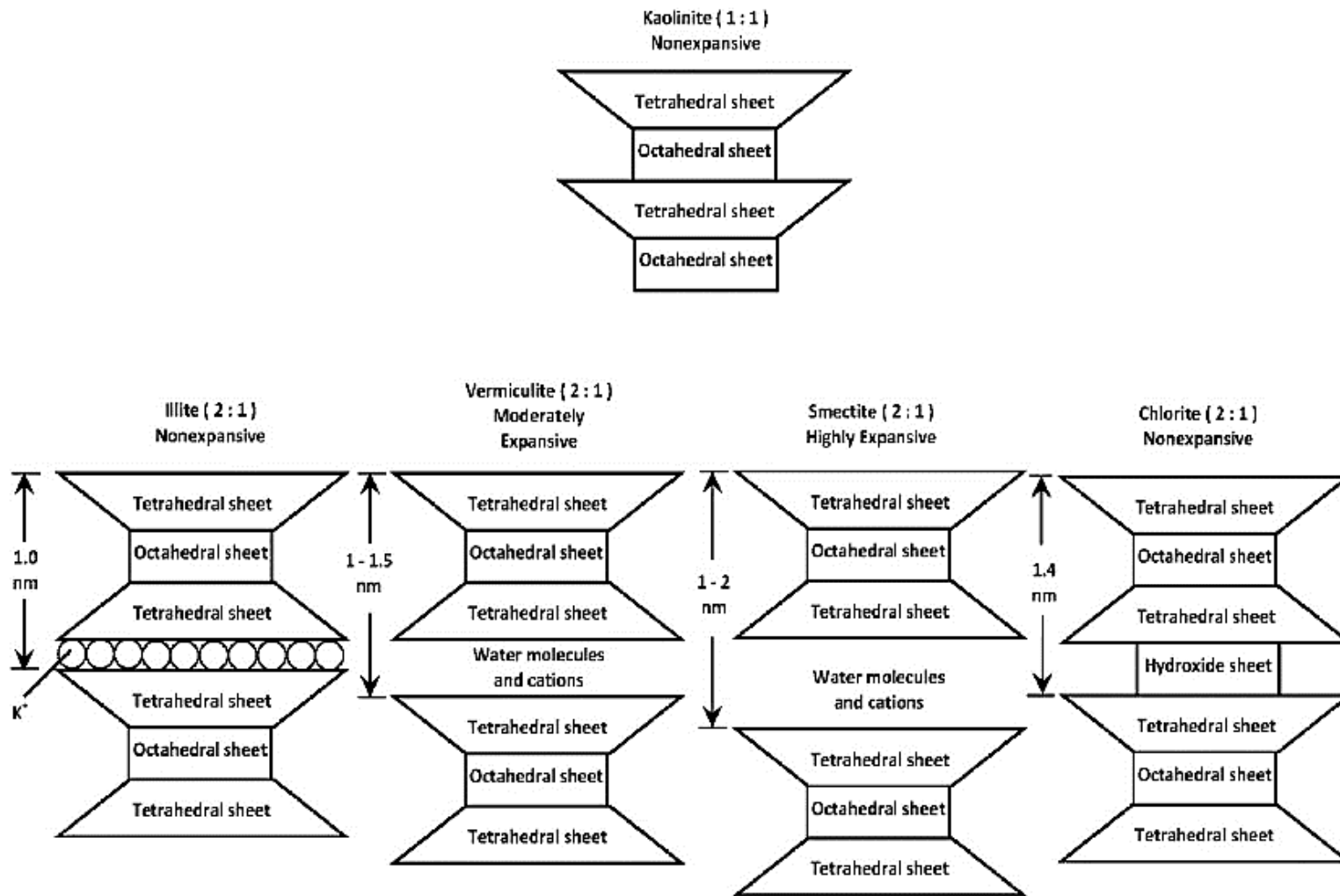
Figure 2.4: Five types of clay minerals based on bonding of their fundamental structures [67]

The presence of exchangeable cations such as sodium (Na^+) located between the interlayers allows the clay to expand when hydrated. This swelling and contraction are unique characteristics found in smectites, which are also the major reasons for smectite clay to be widely used in a range of applications. The weathering of mica replaces the interlayer potassium ions (K^+) with exchangeable cations, leading to vermiculite formation. In soils, vermiculite exists as an Al^{3+} dominated dioctahedral mineral, and to a lesser extent, as a Mg^{2+} dominated trioctahedral mineral. Consequently, vermiculites exhibit a high cation exchange capacity, particularly for weakly hydrated cations such as potassium ion (K^+), ammonium ion (NH^{4+}) and caesium ion (Cs^+). Because of the tetrahedral charge origin, water molecules and exchangeable cations are adsorbed within the interlayer space of vermiculites. However, vermiculites differ from smectite clay due to 2:1 layers being held together by strong bonding of interlayer cations, limiting the swelling of the basal spacing.

2:1:1 clay mineral contains a structure similar to 2:1 layer structure (Figure 2.4), but with an interlayer of gibbsite like sheet. Negative charge arising from 2:1 layers balances the net charge created by isomorphic substitutions within the interlayer hydroxide sheet. A typical formula for the interlayer sheet is $(MgFeAl)(OH)_6^+$. Water adsorption is not present within the interlayer space. Therefore, chlorites are considered as non-expansive minerals.

2.6.3 Properties of bentonite clay

Bentonite is an ore in which the major mineral is montmorillonite. It was discovered in approximately 1890 in the United States, and the name ''bentonite'' is associated with the name of an American geologist from the former Fort Benton in the Rock Creek area of Eastern Wyoming [67]. As mentioned in the classification of clay, bentonite belongs to expandable 2:1 smectite clay mineral (Figure 2.5).
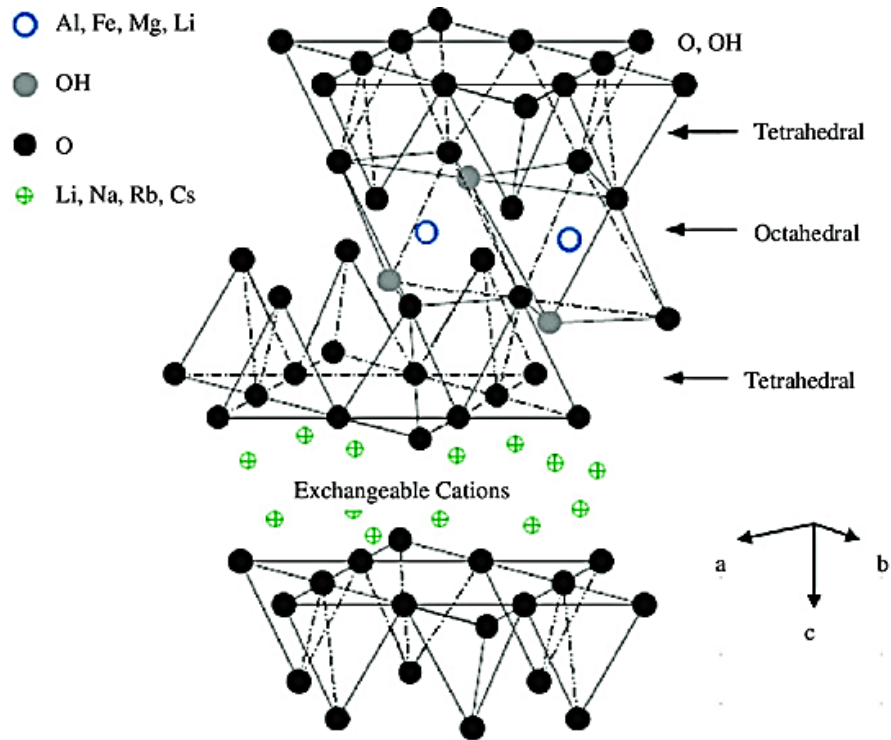
Figure 2.5: Structure of bentonite clay [20]

Clay layers of bentonite are held together by electrostatic forces between the exchangeable cations and the layers, and by van der Waals interactions. In addition, they absorb water through hydration of exchangeable cations, making the clay surfaces hydrophilic. This increases the interlayer distance of the clays, which is known as swelling. Bentonite clay is capable of removing heavy metal cations by replacing exchangeable interlayer cations via cation exchange reaction [68-72]. The hydrophilic nature and the negative charge of clay minerals can be modified by replacing the exchangeable interlayer cations with organic cations (e.g. cationic surfactants) and inorganic cations (e.g. metal poly-cations). The resulting clays are known as organoclays and metal oxide-pillared clays.

2.6.4 Properties of bentonite clay in favour of moisture management property

The most unique property of bentonite clay is its ability to adsorb water between the layers, resulting in strong repulsive forces and clay expansion. This is widely known

for swellable clay. Generally, it has an ability to absorb nearly 5 times its weight in water, and at full saturation may occupy a volume 12 to 15 times its dry bulk [20]. Moreover, bentonite is capable for hydrate and dehydrate an infinite number of times, while preserving its original swelling capacity and original structure. A similar behaviour is observed when frozen and thawed repeatedly. The high water absorption capacity of bentonite also makes it very flexible and resistant to deformations. In addition to that, bentonite possesses two types of surfaces, edges and basal planes, as shown in Figure 2.6. On these edges, there are hydroxyl groups which can easily react with molecules. Further, these OH$^-$ groups make bentonite more hydrophilic.
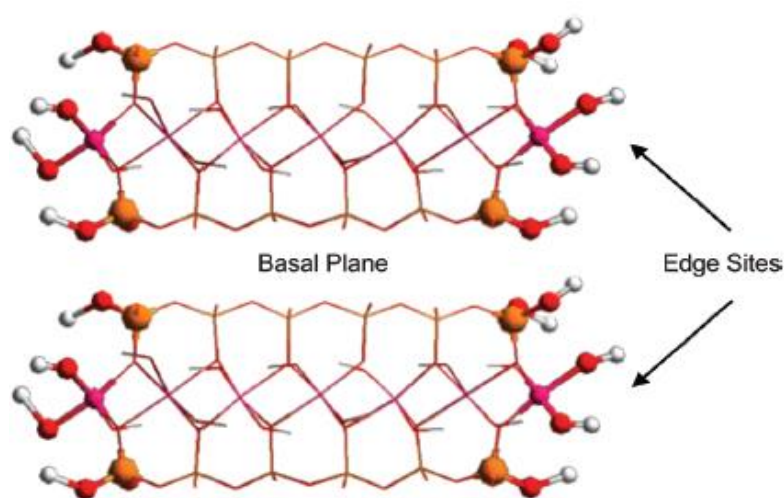
Figure 2.6: Hydroxyl groups on edges of bentonite clay [73]

Hence, above mentioned properties such as high swelling capacity, shrink-swell ability and hydroxyl bonds of bentonite clay are suitable for moisture absorption, while its porosity enhances the moisture evaporation.

2.7   Functionalization of textiles with clay

This section covers finding of novel clay modification for polyester to enhance its moisture management, which in turn bridges the gap in existing literature.

2.7.1　Silane coupling agent

Monometric silicon chemicals are known as silanes. A silane that contains at least one silicon-carbon bond structure is known as organosilane. The organosilane molecule (Figure 2.7) has two key elements [74].
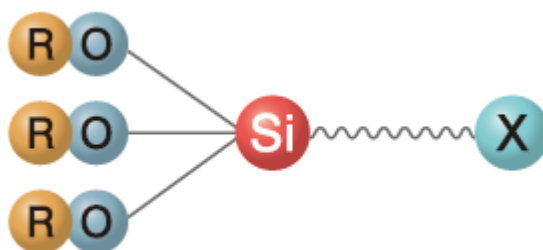
Figure 2.7: The basic molecular structure of silane coupling agent

OR is a hydrolysable alkoxy group (such as methoxy, ethoxy or acetoxy groups), which is very sensitive to moisture. It can react with various forms of hydroxyl groups present in desirable substances (mineral fillers or polymers), and liberates alcohols or acid as a by-product. X is a non-hydrolysable organic part, which can be amino, epoxy, vinyl, methacrylate or sulphur. This part can be reactive towards another chemical. These groups can provide the linkage with inorganic or organic substrates. There is a spacer group between X and Si, which can be either an aryl or an alkyl chain, typically propyl.

Through their dual reactivity, organosilanes (Figure 2.8) serve as links between inorganic substrates such as minerals, cellulose, fillers and metals, and organic or polymers such as rubber and thermoplastics. This can dramatically improve the adhesion between them [75].
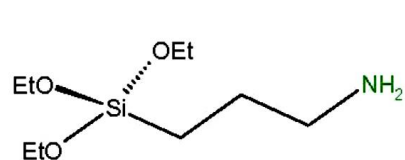
Amino-silane
γ-Aminopropyltriethoxysilane
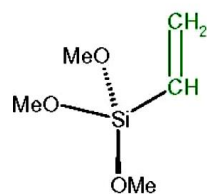
Vinyl-silane
Vinyltrimethoxysilane
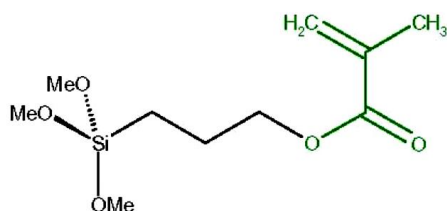
Methacryloxy-silane
γ-Methacryloxypropyltrimethoxysilane
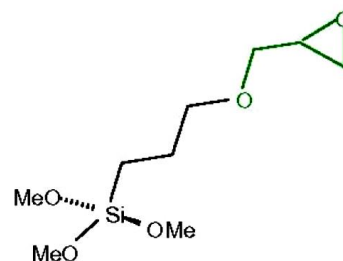
Epoxy-silane
γ-Glycidoxypropyltrimethoxysilane

Figure 2.8: Different types of silane coupling agents

2.7.2 Functionalization of clay and polyester with coupling agent

APTES (Figure 2.9) is an amino-functional silane, which has many advantages compared to other silane coupling agents [76]. APTES freely dissolves in water, where its alkalinity catalyses the hydrolysis. Hence, neutral water is used by aminosilanes for hydrolysis. Due to high moisture sensitivity of silane, the hydrolysis immediately takes place when it contacts water. Immediate condensation occurs between silanols due to their instability in alkaline media. For a few percent by weight of neutral silane solution, nearly all of silane molecules are silanetriol. On the other hand, the same concentration of an aminosilane yields a solution with nearly 100% oligomeric silanes. If the silane concentration in water is significantly low, the content of monomeric aminosilanetriol dramatically increases. When increasing the concentration of hydrolysed silane, the size of silane increases from silanetriols to oligomeric silanes by condensation. The structures formed by condensation of silanols are more complex, since the silanetriol can lead to many possible structures. When silane coupling agents react with desirable substances or surfaces, a similar

condensation reaction takes place with the hydrolysed silanols and the hydroxyl groups of desirable substance, allowing the silane to bind chemically to the surface. In literature, a range of inorganic surfaces which have hydroxyl groups have been coupled with suitable silane coupling agents. [77-80]. For instance, APTES has been used immobilized on polyester surface, as it has an amine group which could react with ester bonds. Further, epoxy containing silane coupling agents such as (3-glycidoxypropyl) trimethoxysilane have been used to react with hydrophilic or hydrophobic moieties to satisfy various needs in many applications [81]. The hydrolysis rate of silane depends strongly on the solvent and pH, and the condensation of silanol to siloxane depends mainly on the pH, temperature and concentration of the solution.
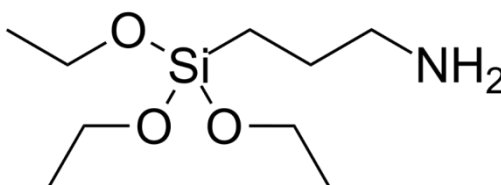
Figure 2.9: Molecular structure of APTES

2.8   Modification of fabrics with clay

In many studies, montmorillonite was applied on fabrics using some chemical and physical methods via electrostatic attraction or hydrogen bonding, to enhance fabric properties such as dyeability, fire-retardancy, uv-protection and mechanical strength [82]. However, above attraction forces are not sufficient to withstand the washing a fabric undergoes after wearing. Hence, the effect of desirable properties applied to fabrics can diminish after few washes [83]. In most of the research studies, clay has been incorporated to its desirable polymer matrix through exfoliation of clay, since the degree of exfoliation of clay affects the properties of the polymer matrix. Therefore, a better dispersion of clay could be obtained through full exfoliation of clay, in order to gain a clay composite with higher thermal stability. Consequently, exfoliation of clay led to offset the hydrophilicity of clay.

2.9   Summary

This chapter has sought to review the literature that supports the immediate requirement for improving moisture management property of polyester fabrics, in order to understand the contributions and limitations of current research in this area. This has led to the development of an experimental framework to guide the studies. Reported modifications for moisture management of polyester fabrics have several disadvantages over their advantages. It has been reported that clay has been applied on fabrics, in which the expected outcome was not the moisture management property of polyester fabrics. According to the literature, bentonite clay could not be covalently attached onto the surface of polyester fabrics using a simple one step process. Hence, across the literature, characterization of clay treated fabrics intending to moisture management property was not reported. These were identified as limitations to accomplish an industrially sustainable and consumer benign moisture management method for polyester fabrics, which are addressed appropriately in this thesis.

3.   METHODOLOGY

3.1   Introduction

This chapter illustrates the experimental work developed for the systematic study and the analysis of the study. The research was based on quantitative and qualitative methods. Hence, theories and scientific methods were applied in order to achieve research objectives. Subsequently, the results were collected to prove the proposed study. The key important steps applied in the research are mentioned under each section.

3.2   Materials and reagents

White woven 100% polyester fabrics and knitted 100% nylon fabrics were obtained from the Weaving Laboratory, University of Moratuwa. (3-aminopropyl) triethoxysilane (APTES, 99%), hydrophilic bentonite clay, (3-glycidoxypropyl) trimethoxysilane (98%), phosphoric acid (H_3PO_4, 85%), sulphuric acid (H_2SO_4, 99%), potassium permanganate ($KMnO_4$, 99.9%), hydrogen peroxide (H_2O_2, 30%), hydrogen chloride (HCl, 37%), ethanol (C_2H_5OH, 99%), sodium chloride (NaCl, 99%) and sodium hydrosulfite ($Na_2S_2O_4$, 99.9%) were purchased from Sigma Aldrich. All chemicals were used without further purification. Graphite flakes (~150 μm) were purchased from Ashbury Graphite Mills, Inc (Ashbury, NJ).

3.3   Reduction of particle size of clay

A dispersion of bentonite clay was obtained by dissolving 4 g of hydrophilic bentonite nanoclay (Aldrich) in 100 ml of deionized water. Then, prepared dispersion was ground using FRITSCH PULVERISETTE 7 premium line grinder (Figure 3.1). In the grinding process, 5 mm zirconia balls were used to reduce the size of clay particles. Particle size of bentonite clay and ground bentonite clay were characterized using particle size analyser (Malvern Zetasizer-Nano ZS, MAL 1032006).

Figure 3.1: Image of FRITSCH PULVERISETTE 7 premium line grinder

3.4 Characterization of BNC

BNC was characterized using XRD, Transmission electron microscope (TEM) and TGA.

3.4.1 XRD studies

Finely ground dry powder of BNC was characterized using XRD. XRD profiles were recorded on a Bruker PW 1050 diffractometer using Cu-Kα radiation (k = 0.154 nm), over a 2θ range of 3°–70°, step size of 0.01, and a step time of 2 s. XRD spectrum and d spacing of BNC were recorded.

3.4.2 TEM studies

TEM analysis was carried out using JEOL JEM 2100 microscope, operating at 200 keV. The BNC was dispersed in water using ultrasonication for 5 min. The suspended BNC was loaded on lacey carbon-coated copper grid, and the sample containing grid was dried for 24 h at room temperature prior to observation. Imaging of selected areas and lattice profiles were recorded.

3.4.3 TGA studies

Finely powdered 12.33 mg of BNC was characterized using thermoanalyser. TGA was carried out on an SDT Q600 thermoanalyser (TA Instrument, sample mass ~10 mg; heating rate 10 °C/min; nitrogen flow). The thermograms and derivative thermograms of BNC were recorded.

3.5 BNC functionalization with coupling agent

A dispersion of 5 g of BNC in 100 ml of deionized water was prepared. Then, 2 mmoldm^{-3} of APTES solution was added to BNC dispersion by controlled dropwise addition. A precipitation was obtained by 1 ml/min drop rate addition of BNC to APTES solution, without agitation in an ambient environment. The slurry was immediately centrifuged (Sigma 3–18) at 9000 rpm for 15 min, and washed five times with deionized water. The collected solid was finally dried at 110 °C for 6 h.

3.6 Characterization of APTES modified BNC

APTES modified BNC was characterized using X-ray photoelectron spectroscopy (XPS), FTIR, XRD, SEM and TGA.

3.6.1 XPS studies

XPS experiments were carried out using a Scienta ESCA 200 spectrometer in ultrahigh vacuum with a base pressure of 1×10^{-10} mbar. The measurement chamber was equipped with a monochromatic Al (K alpha) x-ray source, providing photons with 1486.6 eV for XPS. The XPS experimental condition was set so, that the full width at half maximum of the clean Au 4f7/2 line (at the binding energy of 84.0 eV) was 0.65 eV. All spectra were measured at a photoelectron take-off angle of 0° (normal emission). To compensate the charge problem in the insulating sample, an electron flood gun was used during XPS measurement to neutralize the sample, in which the C 1s was set at 285.0 eV.

3.6.2 FTIR studies

Finely ground BNC and APTES modified BNC samples were characterized using Fourier transform infrared spectrophotometry (FTIR). FTIR spectra were obtained on a Bruker Vertex 80 coupled with Ram-FT module (RAM II, DTGS detector, 4000–400 cm^{-1} spectral range, resolution of 4 cm^{-1}, OPUS software).

3.6.3 XRD studies

Finely ground APTES modified BNC powder was characterized using XRD similar to Sub-section 3.4.1.

3.6.4 SEM and EDX studies

SEM and Energy dispersive x-ray spectroscopy (EDX) analysis were recorded using HITACHI SU6600 microscope, coupled with EDX detector. The samples were coated with gold prior to analysis. The images were recorded.

3.6.5 TGA studies

Finely ground APTES modified BNC powder and liquid APTES were characterized using TGA similar to Sub-section 3.4.3.

3.7 Polyester fabrics

Woven, non-dyed polyester fabric was purified with a detergent, while boiling for 30 min. Then, washed sample was dried at 110 °C for 1 h. Cleaned fabric was characterized and used for modifications.

3.8 Reaction of polyester fabrics with APTES

Using controlled drop wise addition of APTES (Aldrich 99%) to deionized water, a 2 mmoldm^{-3} solution was prepared and stirred it for 30 min. Then, purified polyester fabric was dipped and stirred in hydrolysed APTES solution at 80 °C for 1.5 h. Dipped fabric was padded and cured at 110 °C and washed thoroughly. Finally, dried sample was used for characterization.

3.9 Characterization of APTES modified polyester

APTES modified polyester was characterized using XPS, FTIR and SEM.

3.9.1 XPS studies

Pristine polyester and APTES modified polyester were characterized using XPS similar to Sub-section 3.6.1.

3.9.2 FTIR studies

Pristine polyester and APTES modified polyester were characterized using FTIR similar to Sub-section 3.6.2.

3.9.3 SEM and EDX studies

Pristine polyester and APTES modified polyester were characterized using SEM and EDX similar to Sub-section 3.6.4.

3.10 Grafting of BNC on APTES modified polyester fabric

APTES modified polyester fabric was dipped in a dispersion of BNC for 1 h. Dipped fabric was padded and cured at 110 ºC and washed thoroughly. Finally, BNC grafted APTES modified polyester was used for characterization.

3.11 Characterization of BNC grafted APTES modified polyester fabric

BNC grafted APTES modified polyester fabric was characterized using XPS, FTIR and SEM.

3.11.1 XPS studies

BNC grafted APTES modified polyester was characterized using XPS similar to Sub-section 3.6.1.

3.11.2 FTIR studies

BNC grafted APTES modified polyester was characterized using FTIR similar to Sub-section 3.6.2.

3.11.3 SEM and EDX studies

BNC grafted APTES modified polyester was characterized using SEM and EDX similar to Sub-section 3.6.4.

3.12 Wash fastness property and abrasion resistance

To understand the stability of BNC on APTES modified fabrics, wash fastness and abrasion resistance tests were done using following methodologies.

3.12.1 Wash fastness property

Wash fastness test was conducted according to the American Association of Textile Chemists and Colorists (AATCC) 61 (2A) standard method. The test was performed using non-ionic detergent and at 50 °C of temperature. In this fabric modification, concentration of Al in BNC was the easiest element to be measured using Agilent 7900 Inductively coupled plasma mass spectrometry (ICP-MS). Hence,

concentration of aluminium in fresh BNC coated on two concentrations of APTES fabrics and same after 5 washes and 10 washes were measured by digesting all these samples. Fabric samples were digested according to the given procedure. 150 mm X 50 mm of a sample was heated at 110 °C for 55 min with 10 ml of 1:5 H_2O_2 (30%)/HNO_3 (70%) acid mixture. The solutions were filled up to 25 ml with deionized water. Then, the solutions were analysed using ICP-MS.

3.12.2 Abrasion resistance

The stability of the coating of BNC for abrasion was measured according to the AATCC 08 method, which resembles the standard test for colour fastness for rubbing in textiles. An abrasion resistance tester was used to carry out this test and James Heal standard abrasive cloth was used to rub against BNC coated fabrics. The sample's size was a circle with 40 mm diameter and three samples from each concentration of APTES were tested. The sample holder is shown in Figure 3.2, which rotates on the standard abrasive cloth. 5000 complete cycles, at a rate of 1 s for each cycle, were abraded against the samples. After that, the abraded cloths were removed from the holders for testing of Al, which has transferred from BNC coated polyester to abraded cloth due to abrasion. Finally, Al content in the abraded standard cloth and un-abraded standard cloth were obtained using X-ray fluorescence (XRF). In XRF analysis, the HROBA XGT-5200 energy dispersive x-ray fluorescence spectrometer was used with 50 kV accelerating voltage and a rhodium anode to generate x-ray radiation.

3.13   Optimization of concentration of APTES on BNC loading

Three sets of each sample as given in Table 3.1 were analysed using TGA similar to Sub-section 3.4.3. The initial weight of each sample was 12 mg. Then the weight of ash in each sample was recorded.
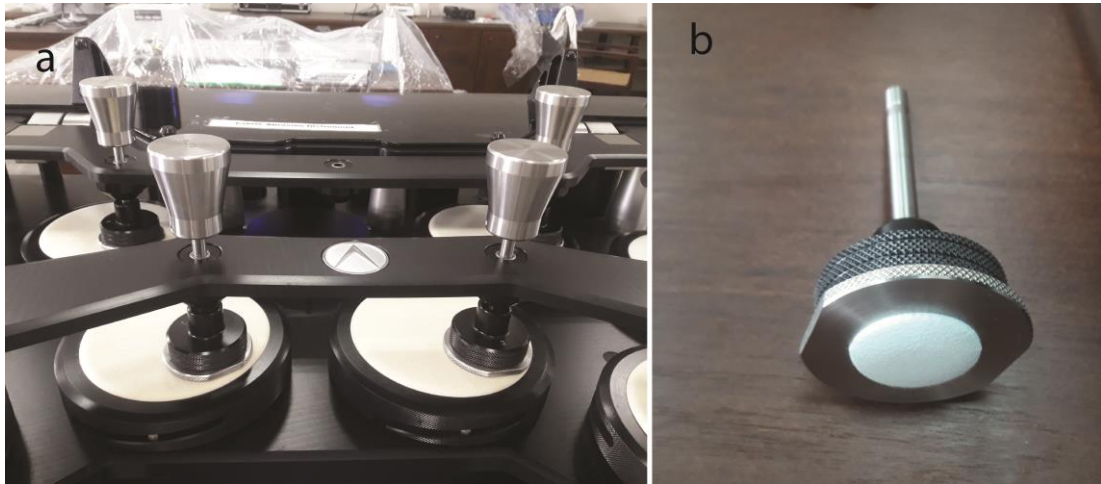
Figure 3.2: Images of (a) abrasion resistance tester, and (b) fabric sample holder

Table 3.1: Fabric samples tested using TGA and XRF

No.	Fabric sample
1	Pristine polyester
2	1 mmoldm^{-3} APTES modified polyester
3	2 mmoldm^{-3} APTES modified polyester
4	3 mmoldm^{-3} APTES modified polyester
5	4 mmoldm^{-3} APTES modified polyester
6	BNC grafted on 1 mmoldm^{-3} APTES modified polyester
7	BNC grafted on 2 mmoldm^{-3} APTES modified polyester
8	BNC grafted on 3 mmoldm^{-3} APTES modified polyester
9	BNC grafted on 4 mmoldm^{-3} APTES modified polyester

The same sets of samples in Table 3.1 were characterized using XRF. Si and Al atomic percentages were recorded for each sample, from three different places of the sample.

3.14   Moisture management testing

All fabric samples were conditioned before testing, for at least 4 h in an atmosphere of 21 ± 1 °C (70 ± 2 °F) and a relative humidity of $65 \pm 2\%$. All tests were performed in the standard atmosphere. Under each moisture management test, 5 samples of pristine polyester, BNC grafted polyester using 1 mmoldm^{-3}, 2 mmoldm^{-3}, 3 mmoldm^{-3} and 4 mmoldm^{-3} of APTES, and 10 times washed BNC grafted samples were tested.

3.14.1 Drop test

In this test, a drop of distilled water from a burette was allowed to fall from a height of 1 cm onto the surface of a fabric sample (10 cm X 10 cm). The time required for specular reflection of the water drop to disappear was measured and recorded as wetting time. It was measured using the standard method AATCC 79-2000.

3.14.2 Absorptive capacity

The absorptive capacity of fabrics was tested using ASTM D1117-80 protocol. A fabric sample of 25 mm X 30 mm was weighed (A) and dipped in distilled water for 5 min, and then hung vertically for another 5 min to allow extra water to drip down. Finally, the fabric sample was weighed again (B) and calculated the water absorptive capacity of the fabric sample using Equation (1).

$$\text{Absorptive capacity (\%)} = \frac{B - A}{A} \text{ X } 100\% \qquad\qquad (1)$$

3.14.3 Drying rate

Size of the fabric sample was 10 cm X 10 cm. The drying rate of fabric was measured by exposing it to 0.01 ml of water, while in contact with a heated plate set to 37 °C (human body perspiring temperature). A test specimen was placed on the heated metal plate for 5 min to allow the specimen to equilibrate to metal plate's temperature. One end of the fabric sample was lifted and 0.01 ml of water was applied on the plate below the fabric. The fabric was repositioned to cover the water drop. The stopwatch was started when the specimen came in contact with the water. An Infar red (IR) camera was used to observe the water drop properly. Finally, the time taken to evaporate the water was recorded. Drying rates were calculated using Equation (2).

$$\text{Drying rate (ml/h)} = \frac{0.01 \text{ ml}}{\text{Drying time (h)}} \qquad\qquad (2)$$

3.14.4 Vertical wicking (warp and weft)

Vertical wicking of fabric samples was carried out according to the AATCC-197-2012 test method (option B – measure distance at a given time). 20 cm X 2.5 cm size samples were cut along the warp and weft directions. A line was marked across each sample at a distance of 5 mm from the end of the fabric. The 5 mm line denotes the level to which a specimen should be lowered into water in the flask or beaker, which is also the test start time. As shown in Figure 3.3, double-sided tape was used to secure the sample to the holder. The rise of water was monitored at 2 min, 5 min and 10 min, and a ruler and IR camera was used to measure the distance that the water has wicked. The distance was recorded in millimetres.

Figure 3.3: Image of carrying out vertical wicking

3.15   Physical properties and tensile strength of fabrics

All fabric samples were conditioned before testing, for at least 4 h in an atmosphere of 21 ± 1 °C (70 ± 2 °F) and a relative humidity of 65 ± 2%. All tests were performed in the standard atmosphere. Under each test, 5 samples of pristine polyester, and BNC grafted polyester using 2 mmoldm^{-3} and 4 mmoldm^{-3} of APTES were tested.

3.15.1 Weight and thickness

The weight per unit area of 100 mm X 100 mm fabric samples were measured using a laboratory electronic weighing balance. Fabric thickness is generally evaluated by measuring the distance between two parallel plates separated by the fabric sample, with a 2 kg weight applied. Thicknesses of the previously weighed samples were measured using a fabric thickness measuring device (Shirley Thickness Gauge, Manchester, UK).

3.15.2 Tensile strength

According to the EN ISO 13934-1:2013 protocol, the strip method was performed using TITAN Universal Strength Tester to determine the tensile strength and breaking elongation of fabric samples. The sample size was 300 mm in length and threaded down to a width of 50 mm. In this method, as illustrated in Figure 3.4, the fabric sample to be tested was gripped by the jaws of the machine. The jaws were typically separated by 200 mm and were pulled at a rate of 100 mm/min. At the point of sample breakage, the maximum force in Newton and the extension of sample in millimetres were read directly from the machine. The average tensile strength was calculated in MPa using the thickness and width of the samples. Average elongation at break was calculated as a percentage of distance between jaws.

Figure 3.4: Image of testing tensile strength of fabric

3.15.3 Air permeability

Air permeability of fabric sample was measured in terms of dm^3/s, using the SDL Atlas M021A Air Permeability Tester according to the ASTM D737 test standard. As shown in Figure 3.5, the specimen was clamped over the test head opening by pressing down the clamping arm, which automatically started the vacuum pump. The pre-selected test pressure was automatically maintained and after a few seconds, the air permeability of test specimen was digitally displayed on the screen. This air permeability was measured at different locations of each sample.

3.15.4 Whiteness index

Fabric samples were evaluated for whiteness index using The Datacolor® 800 Family of Benchtop Spectrophotometers system, as per the CIE whiteness illuminant U3500 10 Deg method.

Figure 3.5: Image of air permeability tester

3.16   Summary

This chapter reported the links between gaps identified from the literature, and converted them into a demanding research design. The novel modification method developed from the literature was elaborated further to prove it quantitatively and qualitatively using characterization techniques such as XPS, FTIR, XRD, SEM, TEM, XRF and TGA. Moisture management tests, and physical and mechanical properties of modified polyester fabric were used to analyse the accomplishment of the modification.

4.   RESULTS AND DISCUSSION

4.1   Introduction

This chapter discusses the results obtained in line with the methodology. Surface modification of polyester fabric is analysed quantitatively and qualitatively using results obtained from XPS, FTIR, XRD, SEM, TEM, XRF and TGA. Concentration of coupling agent was optimized in order to obtain the best moisture management in the modified fabrics. Moisture management test results are analysed to prove the accomplishment of the modification and also its wash fastness properties. Further, physical and mechanical properties of modified fabric are compared with the pristine fabric, to validate the proposed modification in order to commercialize.

4.2   Reduction of particle size of clay

As mentioned in Chapter 2, reducing the length of clay particles in micrometre range leads to increased active surface area (hydroxyl groups) on edges. Abundance of these hydroxyl groups plays a crucial role in this clay modification. Nano grinder reduced the particle size into nano range. Particle size analyser was used to find the average particle size of bentonite clay and ground bentonite clay. The particle size distribution obtained by intensity spectra of bentonite clay (Figure 4.1) showed a broad size distribution ranging from as small as 120 nm to as big as 800 nm particles.

The particle size distribution obtained by intensity spectra of ground bentonite clay (Figure 4.2) showed a size distribution ranging from 100 nm to 120 nm particles. This reduction of particle size decreases the original length of bentonite clay platelets, which increases the edges. This results in increasing hydroxyl groups on edges.
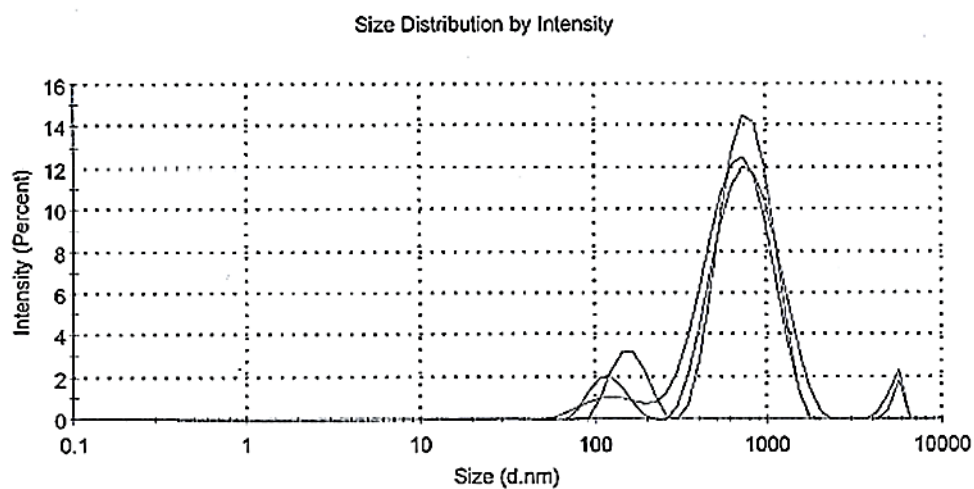
Figure 4.1: Particle size distribution of bentonite clay
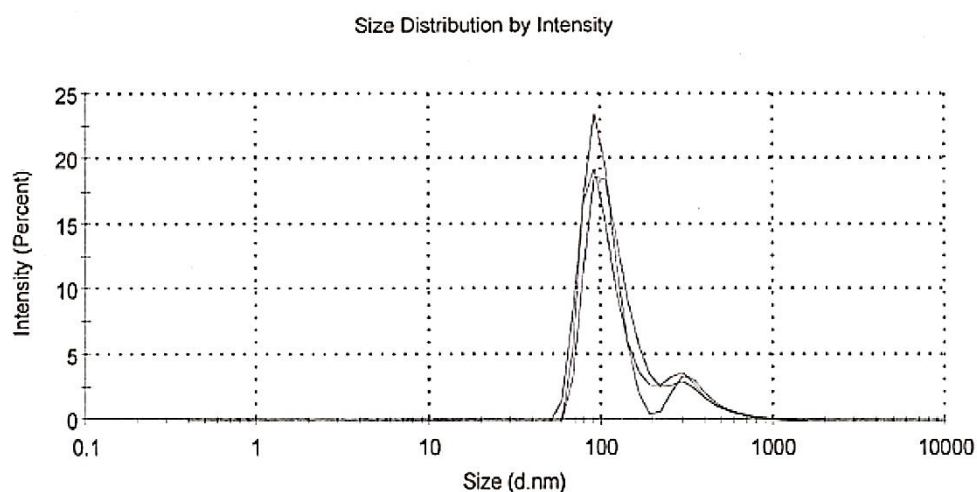
Figure 4.2: Particle size distribution of ground bentonite clay

4.3 Characterization of BNC

Characterized XRD, TEM and TGA results of BNC are discussed in the following sub-sections.

4.3.1 XRD studies

XRD was used to determine basal reflections, which is a major characteristic of BNC. This refers to interlayer distance of BNC. Selected hydrophilic bentonite clay

contained pure bentonite, since it was directly purchased from Sigma Aldrich. Further composition analysis was not needed due to its purity, and more attention was set to determine interlayer distance (basal spacing). XRD spectrum in Figure 4.3 exhibits a peak at $2\theta = 7.8°$ corresponding to the (001) plane, indicating the basal spacing of BNC [84]. According to Bragg's equation ($n\lambda = 2d\sin\theta$), basal spacing of BNC is 1.47 nm. This basal spacing figure plays an important role in this BNC modification, since interlayer distance changes with the modification.
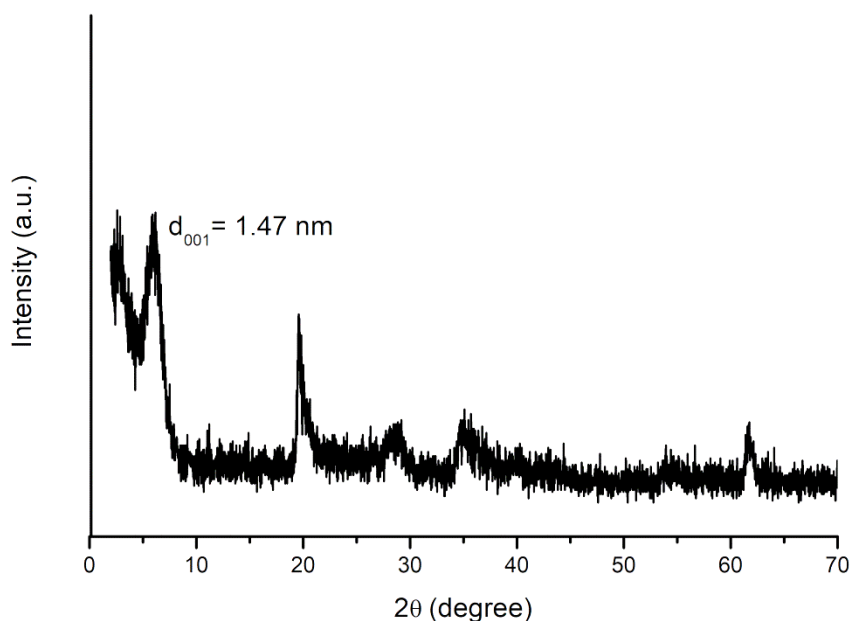
Figure 4.3: XRD spectrum of BNC

4.3.2 TEM studies

Bentonite clay was further analyzed using TEM, which helps to identify interlayer distance and obtain pictures of the lattices. Images in Figure 4.4 (a) and (c) obtained from the edges of BNC show lattice stripes and correspond to the basal planes. The value of the interlayer space for different particles varies within the range from 1.183 nm to 1.906 nm, as shown in lattice profiles of BNC (Figure 4.4 (b) and (d)). The minimum disturbance to the layered structure (minimum exfoliation) of clay during the grinding process was proved using TEM images of BNC.
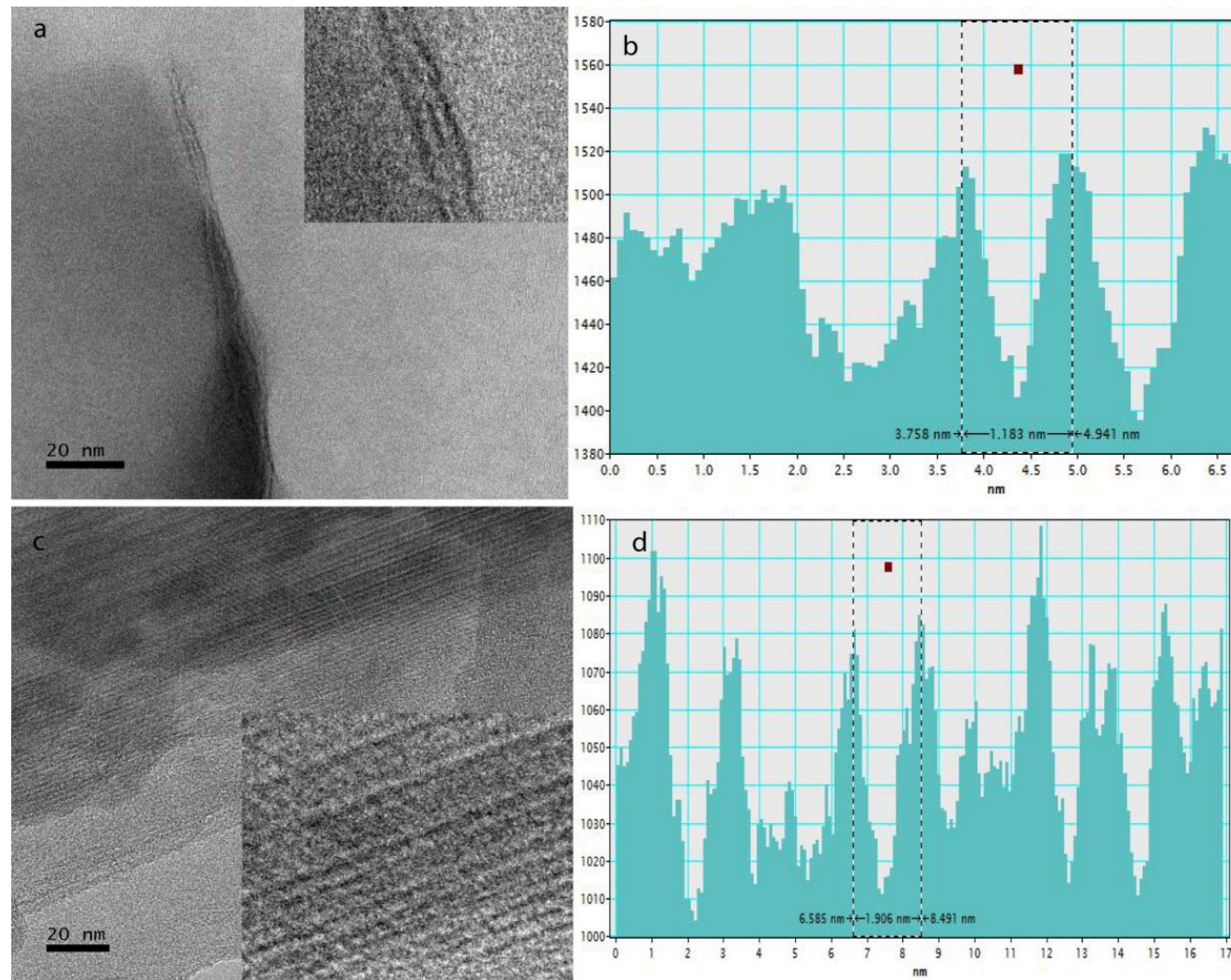
Figure 4.4: (a) and (c) TEM images of BNC, and (b) and (d) lattice profiles of BNC

TEM images in Figure 4.4 show less disturbed layered structure of BNC and interlayer distance. Change in interlayer distance was not significant according to lattice profiles of BNC. The main intention of preserving the structure of BNC was to get its maximum structural benefit in order to obtain its hydrophilicity and swelling properties. If the grinding causes severe damages to the structure of bentonite, its expected properties may disappear. As discussed in Chapter 2, cations in the interlayer greatly contribute to superior water absorption and swelling properties of bentonite clay. Therefore, these results proved that BNC has preserved its important properties.

4.3.3   TGA studies

The thermogravimetric analysis is considered a simple and accurate method to evaluate the thermal stability and decomposition of BNC. The thermogram together with derivative thermogram (DTG) for BNC is shown in Figure 4.5. DTG curve shows weight losses occurring at two distinct temperatures. The first weight loss (14.96%) occurring at 100 °C was attributed to the loss of physically adsorbed water, while the second weight loss (4.17%) occurring at 645 °C was attributed to the dehydroxylation of clay [85]. The weight loss (1.80%) observed in the range 200–500 °C was related to the presence of coordinated water to cations [86].
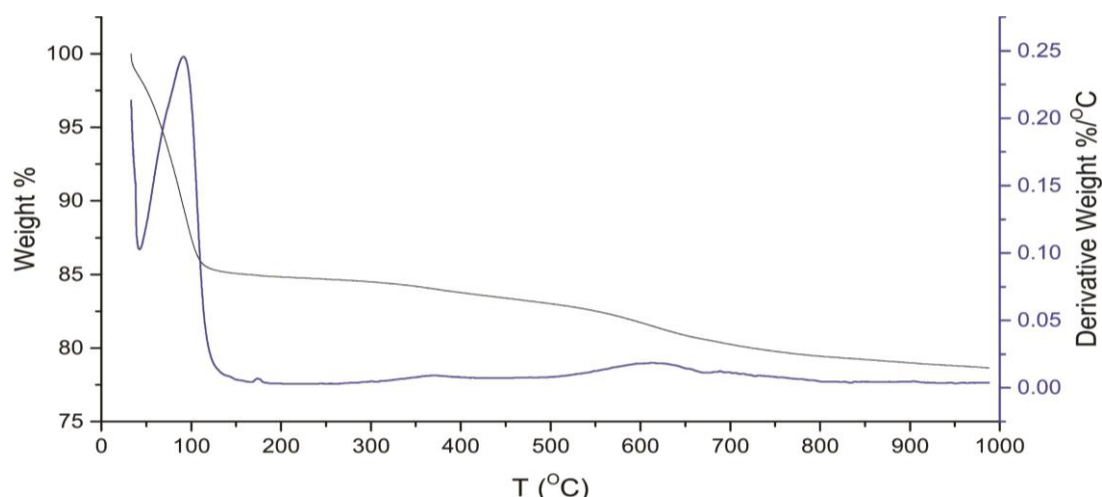
Figure 4.5: (a) The thermogram together with (b) DTG of BNC

4.4   Coupling agent – (3-aminopropyl) triethoxysilane (APTES)

As discussed in Chapter 2, APTES is highly reactive when it is exposed to moisture. APTES is readily hydrolysable due to ethoxy group forming silanol, and by-product ethanol, followed by self-condensation of silanol. Hydrolysing of silanes can be catalysed by acids or alkalis, since most of silanes do not dissolve in water. Due to the presence of amino group in APTES, it was not necessary to add catalysing agent, and the amino group self-catalysed the reaction. Hence, it dissolves in water as soon as it contacts water. Silanols react with each other to form siloxane bonds (Si–O–Si) and finally end up in forming oligomers, which are hydrophobic and insoluble solids. Further, this self-condensation prevents silanol reacting with hydroxyl groups of BNC. To minimize the formation of oligomers, a low concentration was used when dissolving APTES in water. This low concentration prevented forming oligomers, and most of silanols did exist as uncondensed monomers. At low concentration, silanol molecules are far apart, and this leads them to exist in uncondensed state. As shown in Figure 4.6, alkali catalysed hydrolysis involves an attack on silicon by a hydroxyl ion to form a penta-coordinate intermediate, followed by bimolecular displacement of alkoxy by hydroxyl [87]. Any high-electron acceptors grouping next to the Si atom will dramatically increase hydrolysis under basic pH.
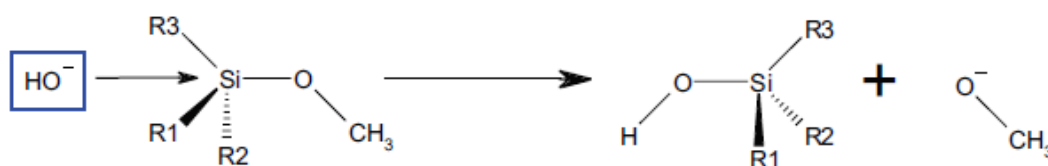
Figure 4.6: Alkali catalysed hydrolysing reaction mechanism of APTES [87]

4.5   BNC functionalization with coupling agent

Bentonite clay in nanoscale increases the hydroxyl groups on the broken edges of its surface, facilitating a rapid reaction with hydrolysed APTES (silylation). Dropwise addition of APTES to deionized water reduces the ability to polymerize the resulted

uncondensed aminopropyl-functional silanetriol monomer. Hence, these uncondensed silanols lead to react with hydroxyl groups on the surface of BNC, forming a stable Si–O–Si bond on drying (Figure 4.7). When a short period of time is given for the reaction in low concentration of APTES, grafting mainly occurs on the broken edges of BNC. As shown in Figure 4.8, hydroxyl groups of BNC reacted with hydrolysed silanols to form H-bonds, followed by forming strong covalent bond Si–O–Si by removing water molecules on heating at 110 °C.
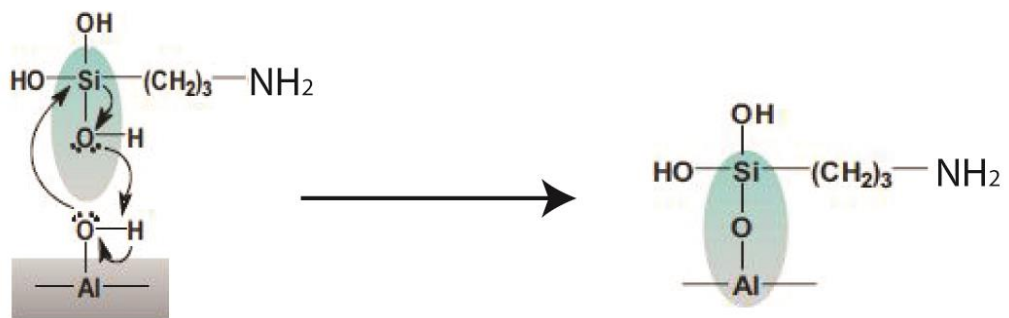
Figure 4.7: Reaction mechanism of forming covalent bond between APTES and BNC
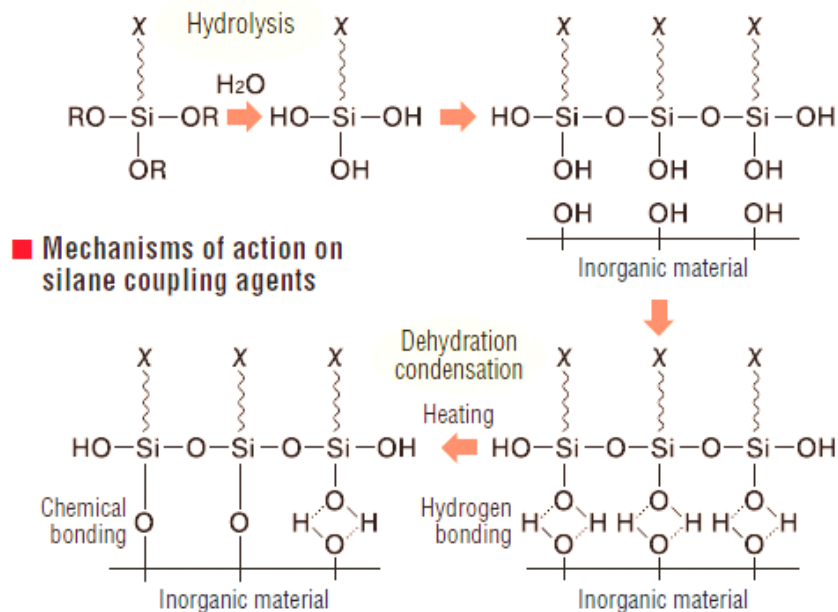
Figure 4.8: Overall reaction mechanism of BNC with hydrolysed APTES [87]

50

4.6   Characterization of APTES modified BNC

This modification was confirmed using characterization data of XPS, FTIR, XRD, SEM and TGA.

4.6.1   XPS studies

XPS is a highly sensitive technique, which is suitable to examine the elemental composition and chemical states of this APTES modified BNC. Further, small changes in the environments of chemical bonding result in small shifts in binding energy. In Table 4.1 and Figure 4.9, the chemical composition and XPS spectra are used to investigate the modification.

Table 4.1 confirmed that APTES modified BNC has significant amounts of nitrogen and carbon, compared to unmodified BNC.

Table 4.1: Elemental composition of BNC and APTES modified BNC from XPS

Sample	Si %	Al %	O %	N %	C %
BNC	26.7	9.7	52.3	0.0	11.3
APTES modified BNC	23.4	6.4	39.6	3.4	27.2

It is clearly visible that Si 2p, Al 2p and O 1s binding energies are present in BNC and APTES modified BNC (Figure 4.9). It can be seen from Figure 4.10 (b) that N 1s binding energy is at 399.95 eV, which is attributed to APTES's primary amine group in APTES modified BNC [85]. The energy difference between Si 2p 3/2 and Si 2p 1/2 levels is ~0.5 eV, causing the two peaks to overlap, giving an asymmetric peak [88]. After the modification, Si 2p binding energy has shifted from 103.5 eV to 102.9 eV, Al 2p from 75.0 eV to 75.2 eV, and O 1s from 532.65 eV to 532.5 eV. These observations are due to the differences in chemical environments (changing the electron density) at the atoms, which induce small chemical shifts broadening the spectra.
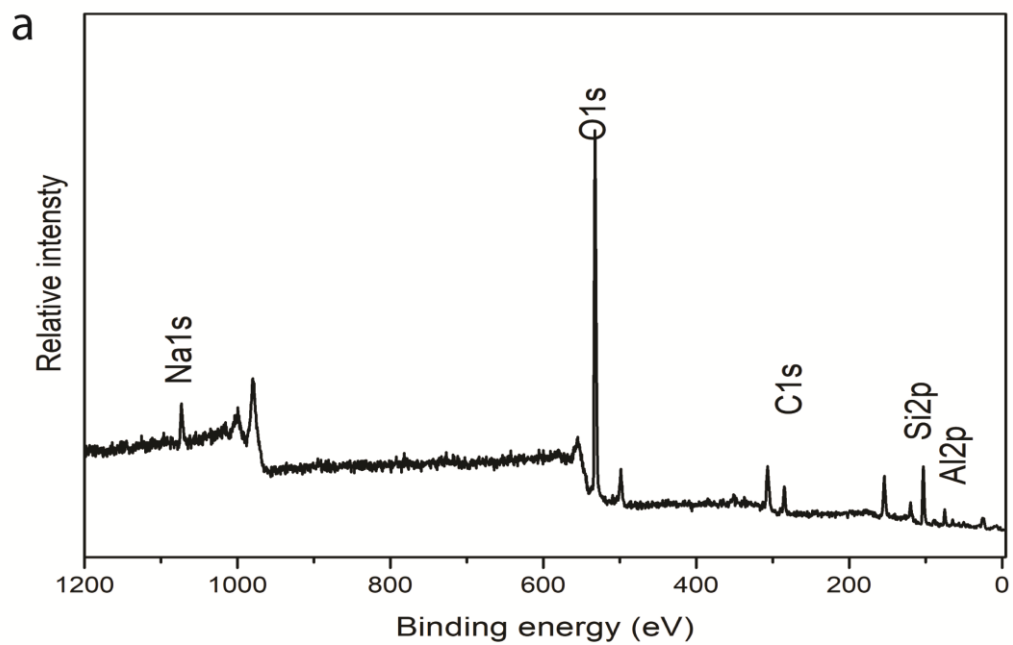
Figure 4.9: XPS spectra of (a) BNC, and (b) APTES modified BNC
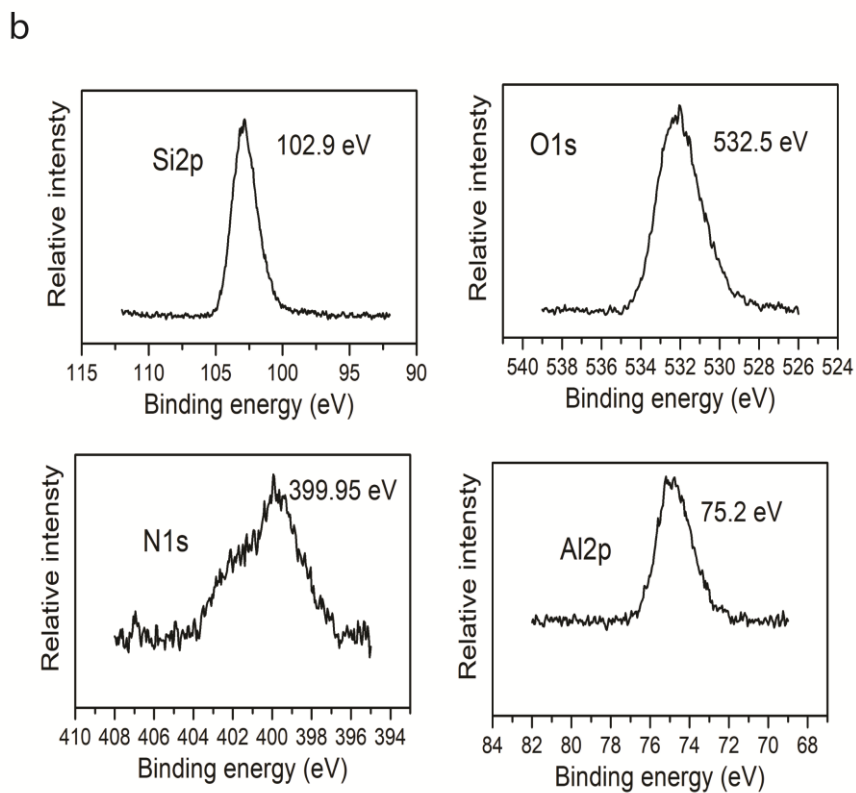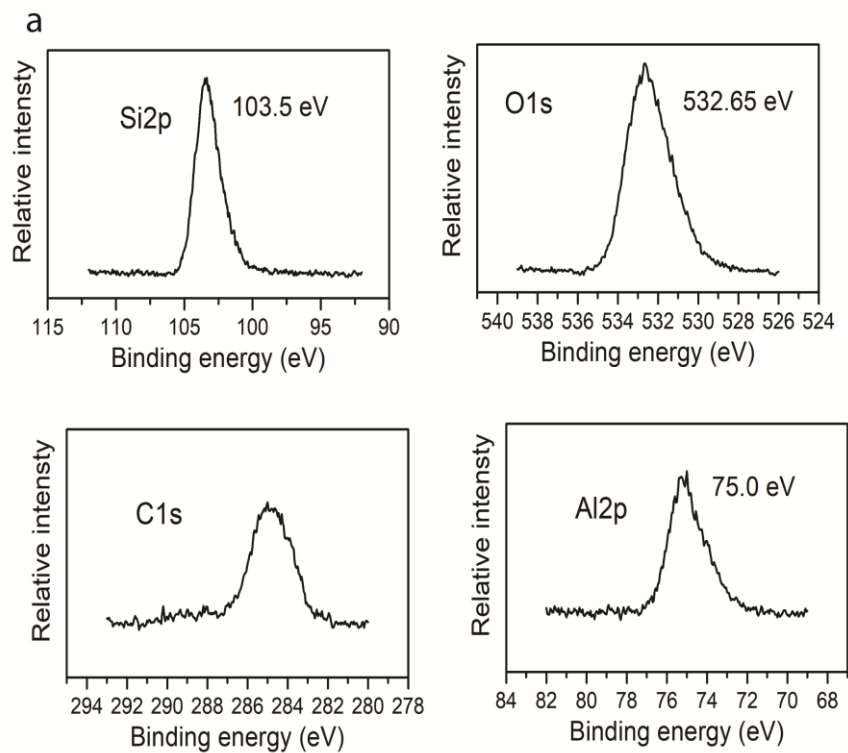
Figure 4.10: Binding energies of (a) BNC, and (b) APTES modified BNC

4.6.2 FTIR studies

FTIR spectra (Figure 4.11) further confirm the formation of bonds between APTES and BNC, by the presence of characteristic absorption bands relevant to bonding of APTES. Successfully grafted APTES on BNC can be confirmed by a group of absorption bands in 3000–2800 cm^{-1} in spectrum (c). This absorption is attributed to the valence vibration ν $_{s,as}$ (CH) of propyl chain in APTES. Its presence is also confirmed by a group of bands of weak intensity in 1490–1300 cm^{-1} region. Spectra (a) and (c) present same set of absorption bands relevant to inorganic structure of BNC [85]. Since modified and non-modified BNC both contain water, there is a characteristic absorption band of deformation vibrations of H$_2$O molecules at 1630 cm^{-1}, and a broad intense absorption band above 3420 cm^{-1} due to vibrations of OH$^-$ groups in water molecules participating in the formation of hydrogen bonds. In spectra (a) and (c), the strong broad band in 1100–900 cm^{-1} is attributed to valence vibration of Si–O bonds in BNC. Moreover, peaks at 3300 cm^{-1}, 700 cm^{-1} and 1340 cm^{-1} correspond to the N–H stretching, C–H bending vibrations and Si–C stretching, respectively. These peaks support the covalent bonding of APTES onto BNC. In spectrum (c), intensive bands in approximately 1200–1100 cm^{-1} represent the asymmetric stretching of siloxane groups (Si–O–Si). These bands correspond to a combination of Si–O–Si vibrational modes, including those of bonds formed between the silane and BNC surface, and cross-linking between silane molecules on the surface [79].
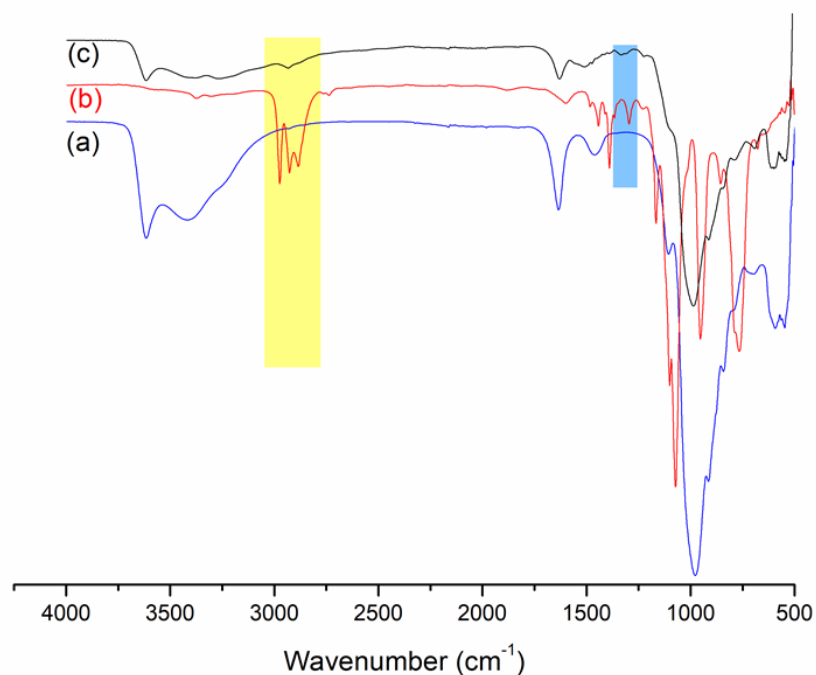
Figure 4.11: FTIR spectra of (a) BNC, (b) APTES, and (c) APTES modified BNC

4.6.3 XRD studies

XRD spectra of BNC (Figure 4.12 (a)) and APTES modified BNC (Figure 4.12 (b)) show no significant shift in the typical peak of (001) plane, which corresponds to the basal spacing of BNC. Spectrum (a) exhibits a peak at $2\theta = 7.8°$ corresponding to the (001) plane, indicating the basal spacing of 1.47 nm. APTES modified BNC (spectrum (b)) exhibits the basal spacing of 1.59 nm. However, the slight shift in the peak of (001) plane in spectrum (b) confirms grafting of APTES on broken edges of BNC. Dropwise addition of APTES to deionized water reduces the ability to polymerize the resulted uncondensed aminopropyl-functional silanetriol monomer. Hence, these uncondensed silanols lead to react with hydroxyl groups on the surface of BNC, forming a stable Si–O–Si bond on drying. When a short period of time is given for the reaction in low concentration of APTES, grafting mainly occurs on the broken edges of BNC. When stirring and increasing the reaction time, grafting reaction occurs not only on the edge, but also in the interlayer nanospace [79].

Further, delayering of BNC can occur under low pH levels. Adjustment of pH was unnecessary, since the alkaline medium created by APTES catalysed the silane grafting process, which was an added advantage in silylation of BNC with APTES.
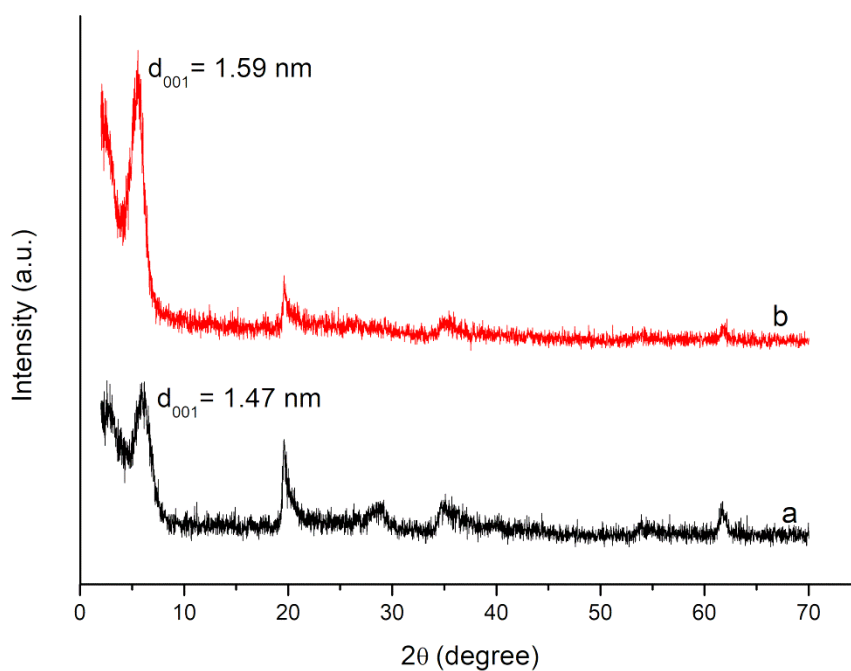
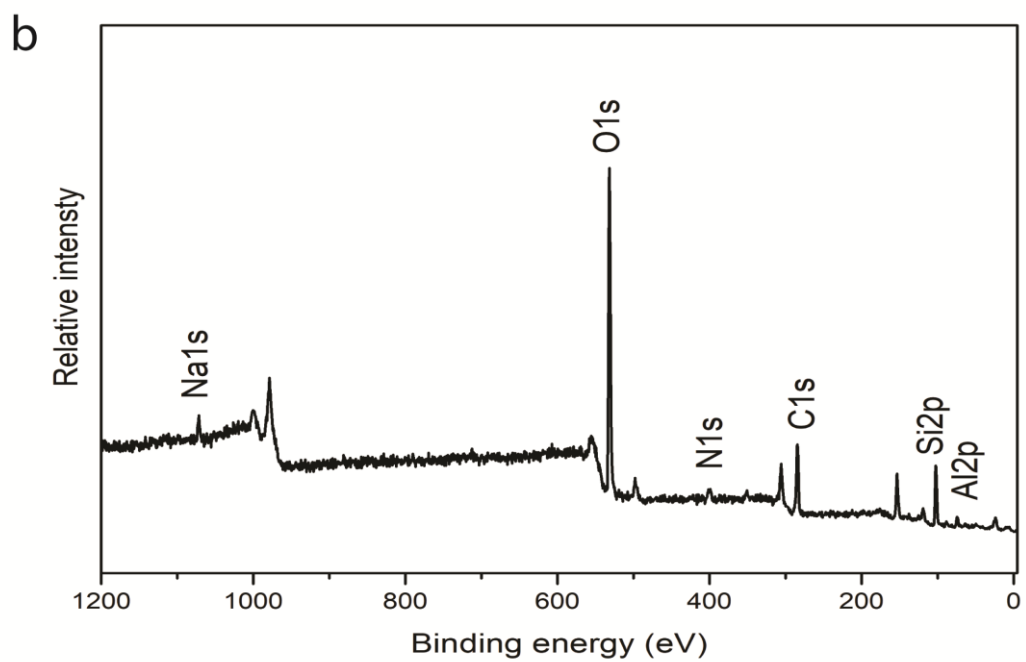Figure 4.12: XRD spectra of (a) BNC, and (b) APTES grafted BNC

4.6.4 SEM and EDX studies

EDX analysis in Figure 4.13 (a) shows the presence of significant amounts of carbon and nitrogen in APTES modified BNC, while the SEM image in Figure 4.13 (b) shows the surface morphology of APTES modified BNC. These figures confirm that APTES has successfully grafted on broken edges of BNC.
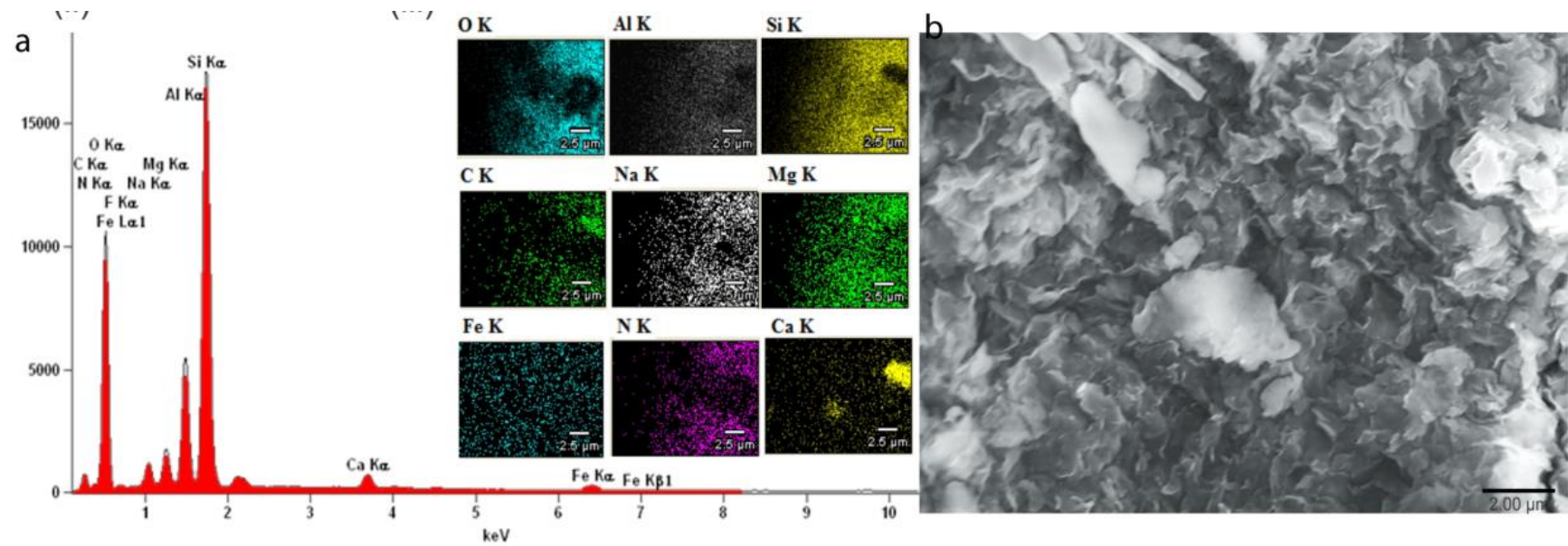
Figure 4.13: (a) EDX spectrum, and (b) SEM image of APTES modified BNC

4.6.5 TGA studies

Thermogravimetric analysis was used to determine the chemically grafted silane on BNC. The thermograms together with derivative thermograms (DTG) for (a) APTES, (b) BNC, and (c) APTES modified BNC are shown in Figure 4.14. DTG curve in graph (b) shows weight losses occurring at two distinct temperatures. The first weight loss (14.96%) occurring at 100 °C was attributed to the loss of physically adsorbed water, while the second weight loss (4.17%) occurring at 645 °C was attributed to the dehydroxylation of BNC [85]. The weight loss (1.80%) observed in the range 200–500 °C was attributed to the dehydroxylation of structural OH^- groups in BNC [85]. After the grafting of APTES, graph (c) shows an initial weight loss (8.56%) taking place up to 150 °C. This can be attributed to the removal of adsorbed surface water. Compared to graph (b), this lesser water content in APTES grafted BNC indicates that APTES has grafted on BNC. The weight loss observed in the range 200–550 °C is mainly attributed to the thermal decomposition of organic molecules [86]. The weight loss (8.49%) observed in the range 400–575 °C corresponds to chemically bonded APTES on broken edges of BNC [89]. As in unmodified BNC, the weight loss (2.92%) observed in the range 600–800 °C is due to the dehydroxylation of BNC. The final weight of APTES modified BNC is greater than unmodified BNC, due to organic and inorganic Si content in APTES.

4.7 Polyester fabrics

In the process of weaving polyester fabrics, chemicals are added to make it easier. Hence, polyester fibre surface is covered with these chemicals, which need to be removed before any modification. To obtain good results, polyester fibre surface should be free of chemicals. After the purification, a cleaned fabric was obtained.
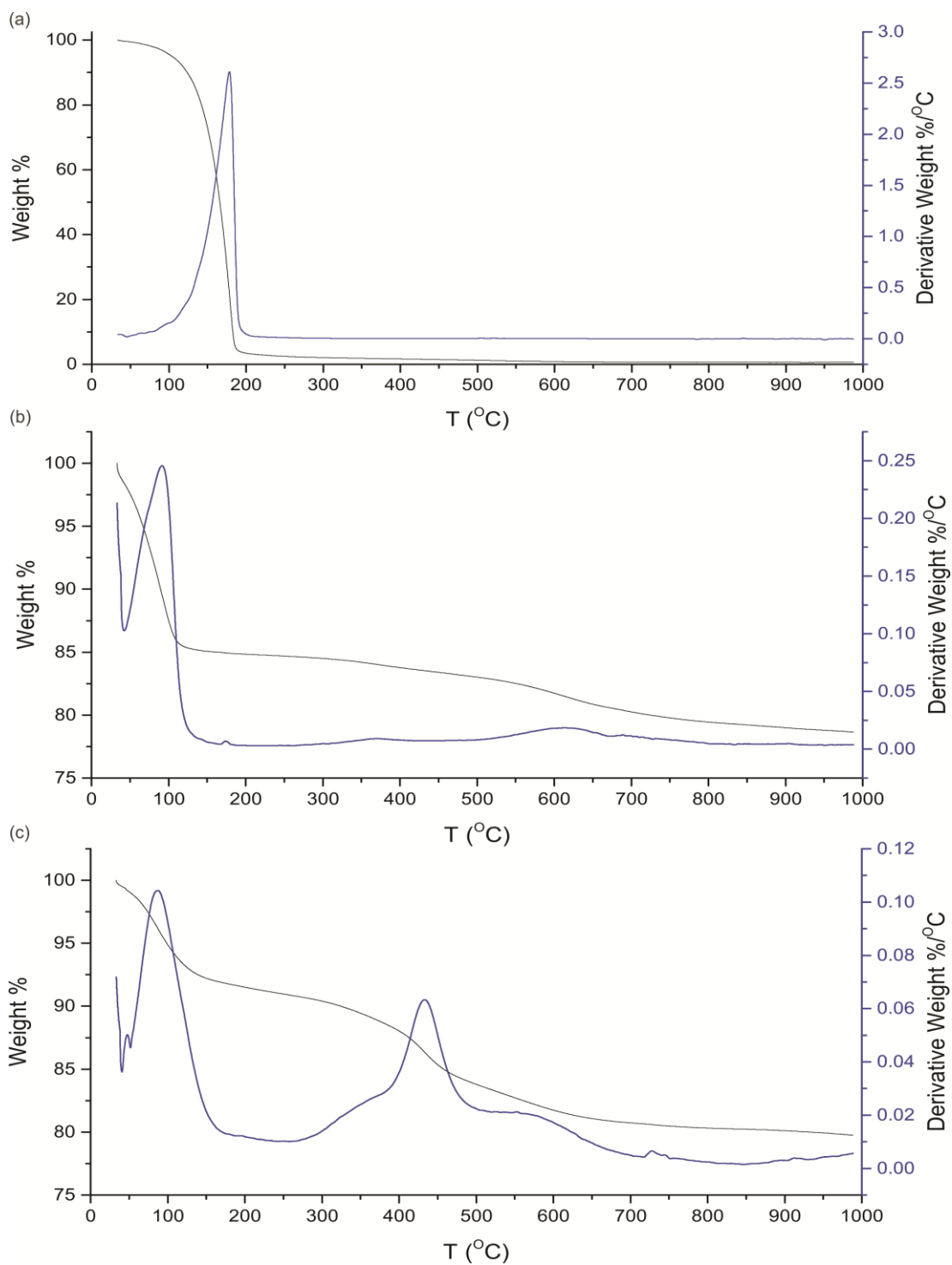
Figure 4.14: The thermograms together with DTG of (a) APTES, (b) BNC, and (c) APTES modified BNC

4.8   Reaction of polyester fabrics with APTES

Firstly, the amino group of APTES reacted with fibres of polyester fabric via nucleophilic attract. Amino group of APTES attacked carbon on ester linkage of polyester to produce secondary amide [90]. The first reaction mechanism is as shown in Figure 4.15.
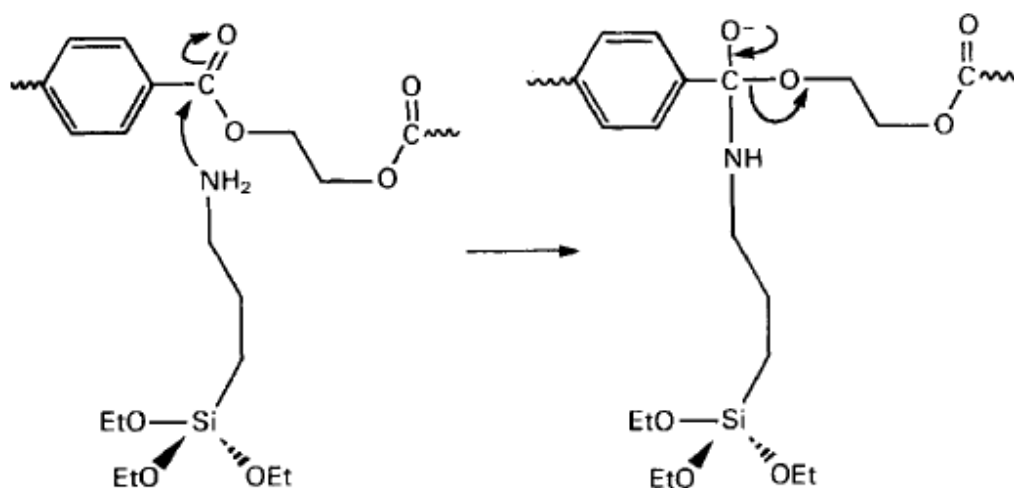
Figure 4.15: Reaction mechanism of APTES and polyester (first step) [90]

However, contrasting to other aminolysis reactions, polyester fabric was free of degradation due to second reaction occurred between the alkoxide group created by the ester cleavage, and APTES. The alkoxide group created by the ester cleavage played an important role in the preservation of the polymeric structure. The substitution reaction between this anion and the silyl end of APTES, which is similar to the reaction between a hydroxyl group and APTES, would have the effect of holding both ends of the ester together. As the negatively charged alkoxide end of the cleaved ester is a much stronger nucleophile than a hydroxyl group, the second reaction was favourable. The proximity of alkoxide moiety to silyl group of the attacking APTES molecule, favours a secondary reaction between these two moieties. This inserted APTES molecule would then cross-link horizontally and

vertically with other APTES molecules near the surface to form the APTES layer. The mechanism of second reaction is as shown in Figure 4.16.
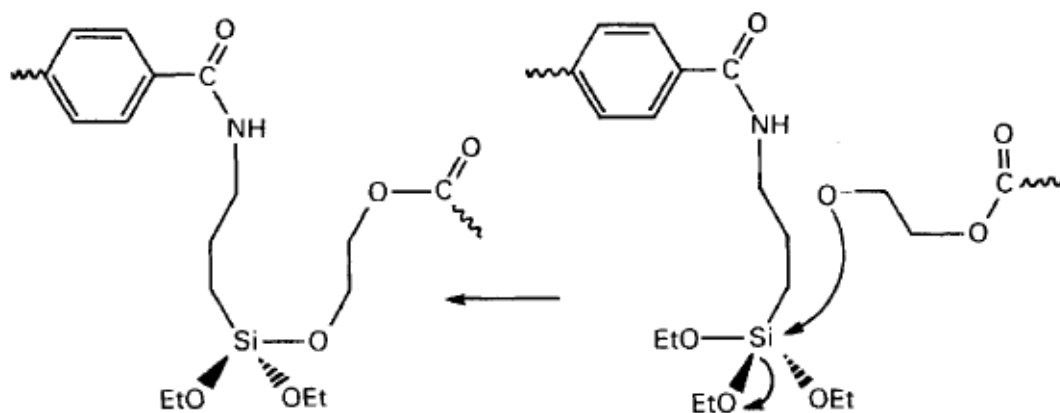
Figure 4.16: Reaction mechanism of APTES and polyester (second step) [90]

4.9 Characterization of APTES modified polyester

Modification of APTES on polyester fabric was confirmed using XPS, FTIR and SEM.

4.9.1 XPS studies

The amide bond formation confirmed using binding energies and chemical composition in XPS data is mentioned in Sub-section 4.11.1.

4.9.2 FTIR studies

The secondary amide bond was confirmed using FTIR spectra in Figure 4.17. Covalent bonding between polyester and APTES modified BNC is confirmed by new absorption peaks in spectrum (B), located at 1645 cm^{-1} [91]. These are attributed to secondary amide groups, formed by direct aminolysis between aminated ends of APTES and surface ester groups of polyester fibres.
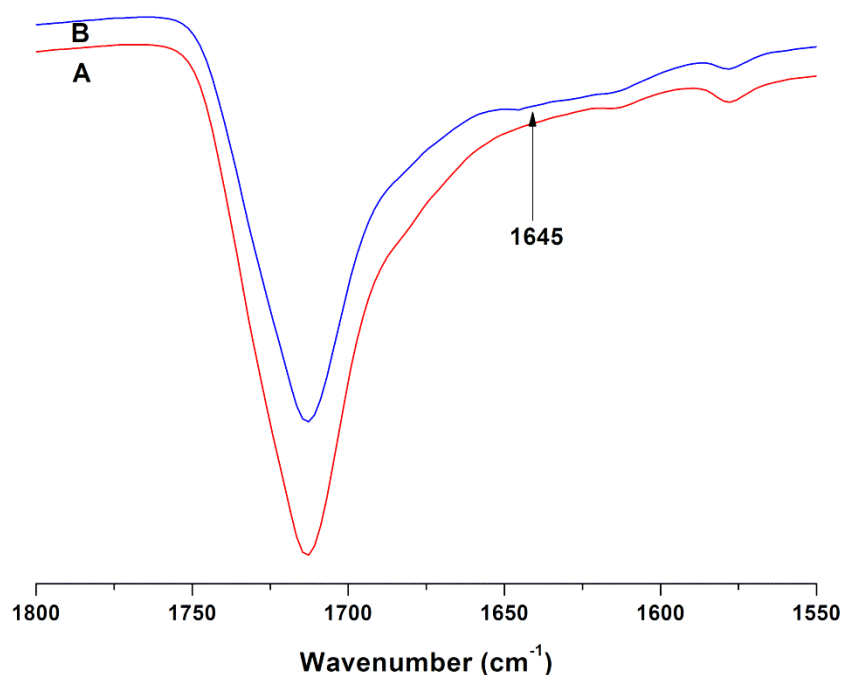
Figure 4.17: FTIR spectra of (A) pristine polyester, and (B) APTES modified polyester

4.9.3 SEM and EDX studies

SEM image of pristine polyester fabric (Figure 4.18 (a)) indicates a smooth fibre surface after the purification. SEM image in Figure 4.18 (b) clearly shows a thin layer of APTES on polyester fibres after being treated with APTES, which is further proved by EDX analysis in Figure 4.19. EDX spectrum shows significant amounts of silicon and nitrogen elements present in APTES modified polyester. These figures confirm evenly grafted APTES on polyester fibre surfaces, which leads to a proper foundation to bind BNC.
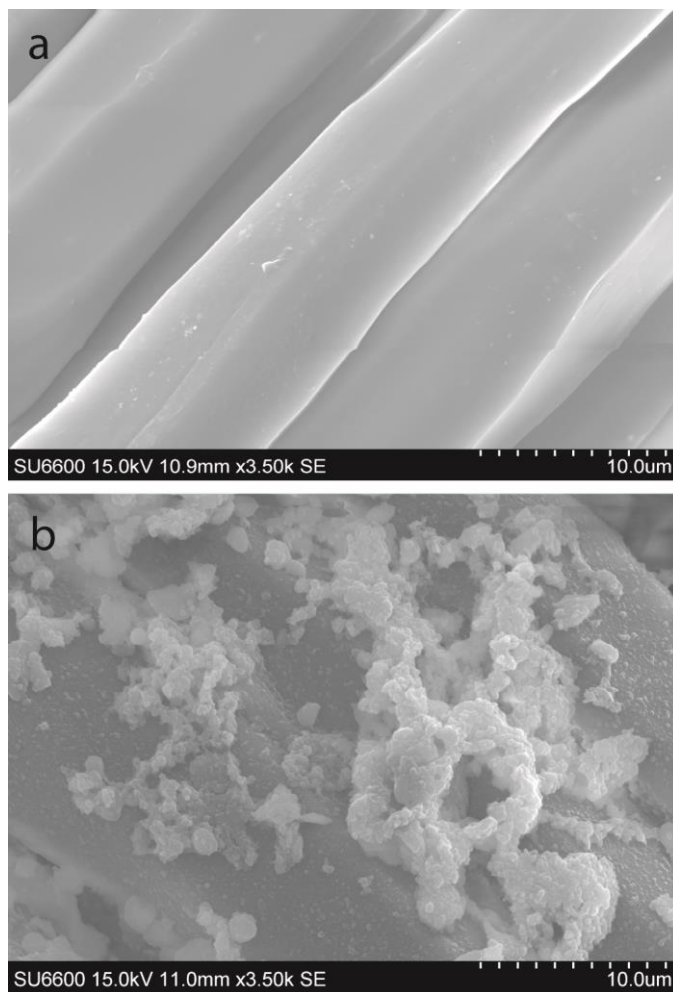
Figure 4.18: SEM images of (a) pristine polyester, and (b) APTES modified polyester
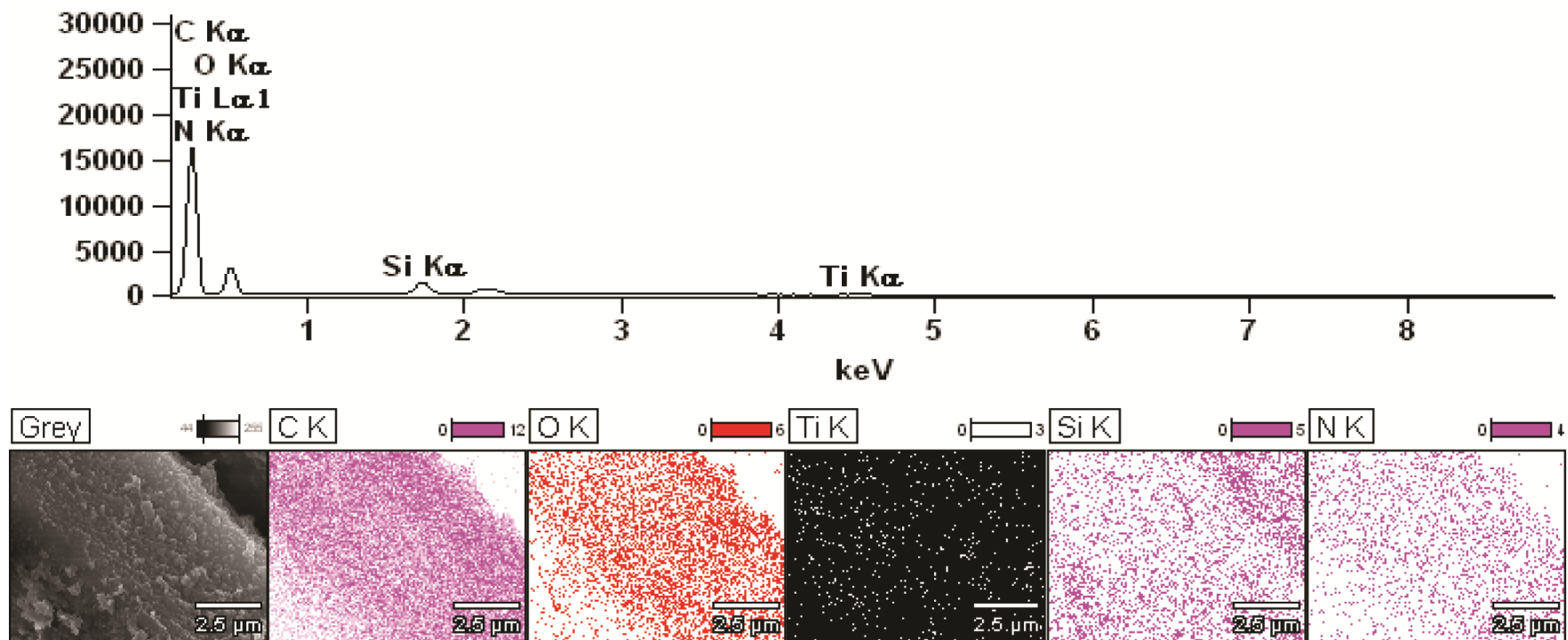
Figure 4.19: EDX spectrum of APTES modified polyester

4.10   Grafting of BNC on APTES modified polyester fabric

As discussed in Chapter 2, hydroxyl groups of BNC reacted with hydrolysed APTES forming hydrogen bonds, followed by Si–O–Si bonds on heating. Schematic diagram of BNC grafted APTES modified polyester fabric is given in Figure 4.20.
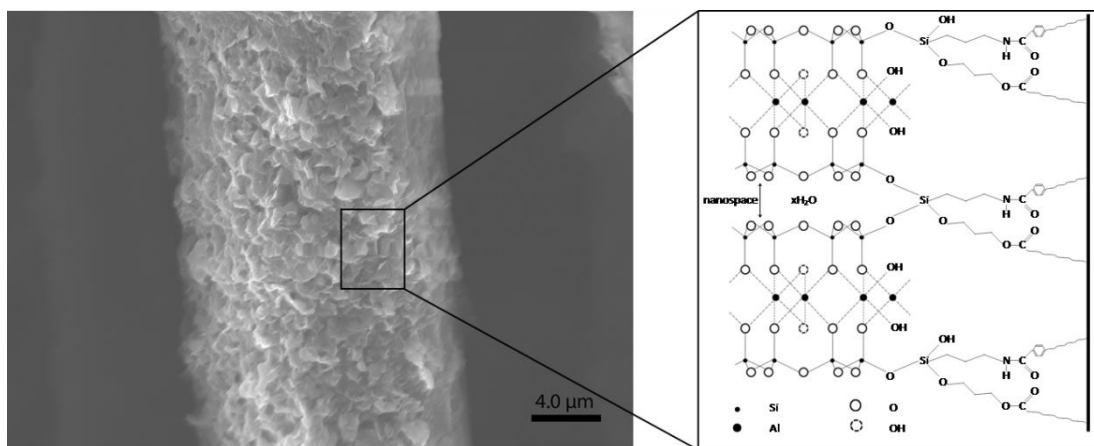
Figure 4.20: Schematic diagram of BNC grafted APTES modified polyester fabric

4.11   Characterization of BNC grafted APTES modified polyester fabric

Grafting of BNC on polyester fabric was proved using XPS and FTIR spectra, and SEM images.

4.11.1 XPS studies

As shown in Table 4.2, after the modification of polyester with APTES, there are significant amounts of Si and N. After grafting BNC on top of modified polyester, a considerable amount of Al is shown in its elemental composition. Further, the amount of O has increased in comparison to APTES modified polyester, due to O content in BNC. Hence, this table clearly confirmed the change in elemental composition upon each modification.

Table 4.2: Elemental composition of pristine polyester, APTES modified polyester, and BNC grafted APTES modified polyester

Fabric sample	C %	O %	Si %	N %	Al %
Pristine polyester	77.1	22.9	0.0	0.0	0.0
APTES modified polyester	64.8	18.5	13.6	3.1	0.0
BNC grafted APTES modified polyester	14.3	46.2	27.6	0.8	11.0

It is clearly observed in Figure 4.21 and Figure 4.22 spectrum (b) that a new binding energy for Si 2p has appeared after treating with APTES. In spectrum (c), a new binding energy for Al 2p has appeared after grafting BNC. The new amide bond formation in modified polyester fabrics was visible through changes in the chemical bonding environments, resulting in small shifts in binding energies. The peak arising from the C–N/N–C=O nitrogens occurs at 402.2 eV, which is attributed to the newly formed amide bonds [92]. Further, C 1s binding energy in spectra (c) displays a shift in the peak from 284.0 eV to 286.8 eV, corresponding to conversion from O–C=O/C–O to C–N/N–C=O [92].

4.11.2 FTIR studies

The appearance of a new broad intense absorption band above 3420 cm^{-1} and a characteristic absorption band at 1630 cm^{-1} in Figure 4.23 spectra (b) and (c) are attributed to vibrations of OH^{-} groups in water molecules of BNC, participating in the formation of hydrogen bonds and deformation vibrations of water molecules, respectively [79]. These absorption bands prove hydrophilicity of BNC coating on the polyester fabric. Further, absorption bands in 1200–1000 cm^{-1} in spectra (b) and (c) are attributed to valence vibration of Si–O and asymmetric stretching of siloxane groups in BNC.
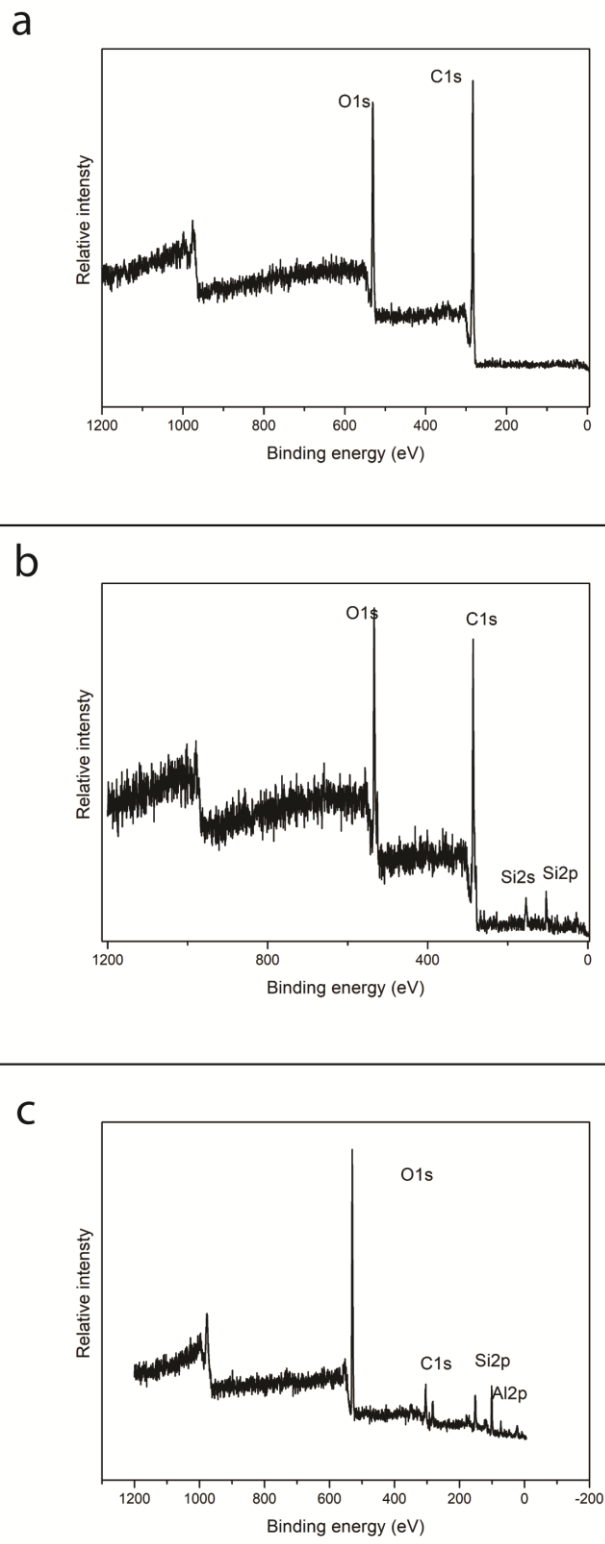
Figure 4.21: XPS spectra of (a) pristine polyester, (b) APTES modified polyester, and (c) BNC grafted APTES modified polyester
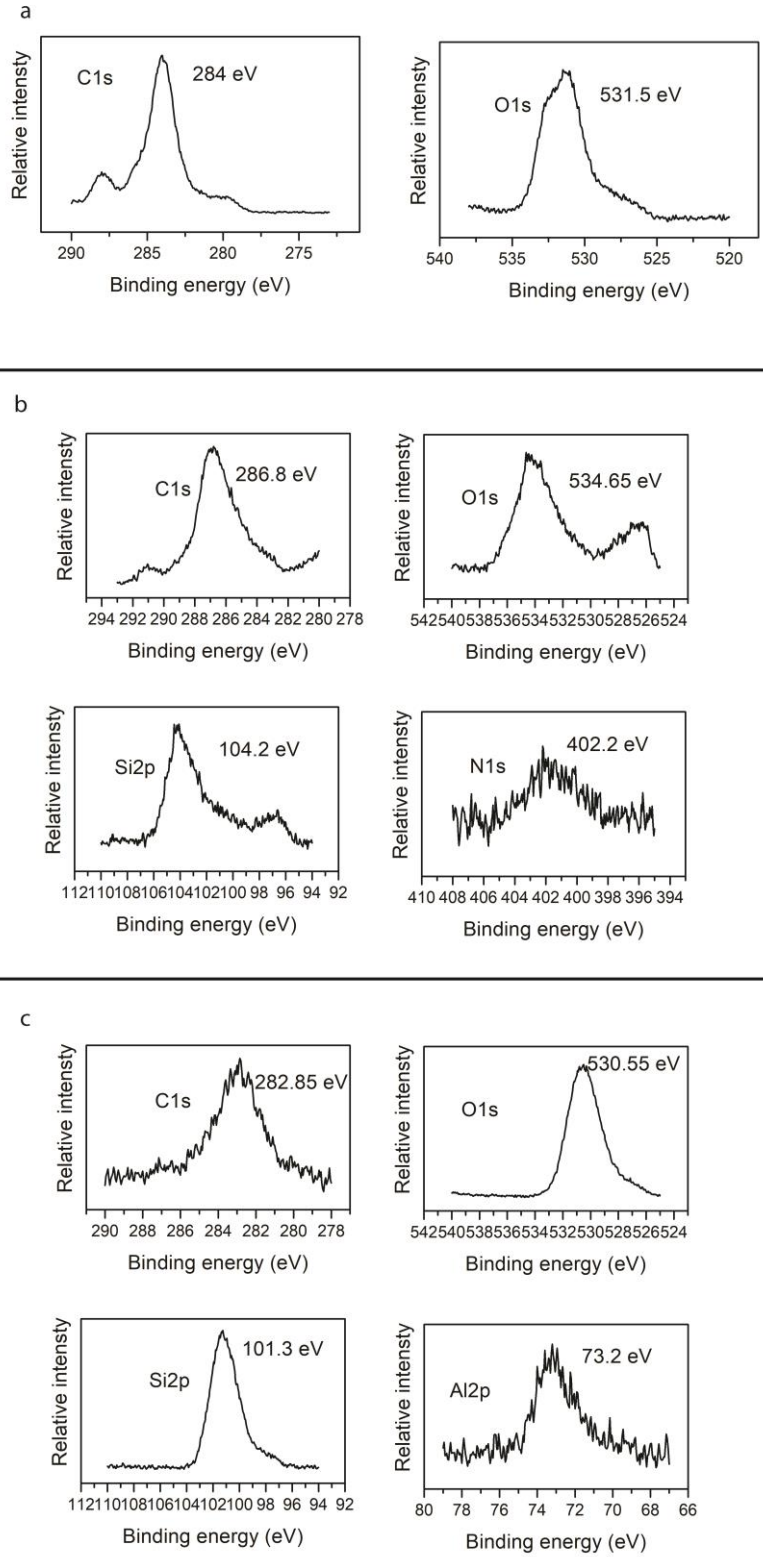
Figure 4.22: Binding energies of (a) pristine polyester, (b) APTES modified polyester, and (c) BNC grafted APTES modified polyester
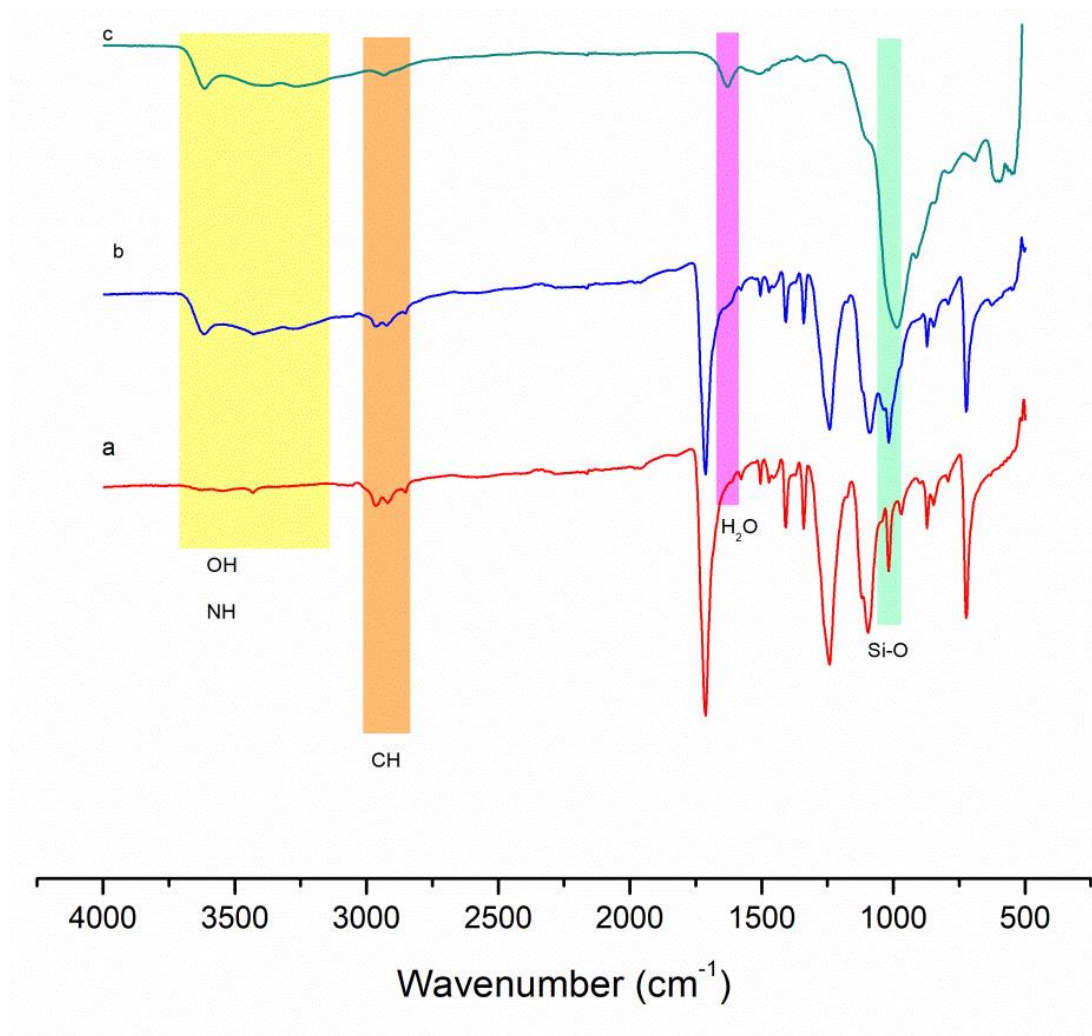
Figure 4.23: FTIR spectra of (a) APTES, (b) BNC grafted APTES modified polyester, and (c) APTES modified BNC

4.11.3 SEM and EDX studies

SEM image of pristine polyester fabric (Figure 4.24 (i) (A)) indicates a smooth fibre surface after the purification. SEM images in Figure 4.24 (i) (B) and (C) clearly show a thin layer of BNC on polyester fibres after being treated with APTES modified BNC, which is further proved by EDX analysis in Figure 4.24 (ii). EDX spectrum shows significant amounts of silicon, aluminium, calcium, sodium and magnesium elements present in BNC grafted polyester. These SEM images confirm evenly grafted BNC on polyester fibre surfaces, which leads to its superior wettability.
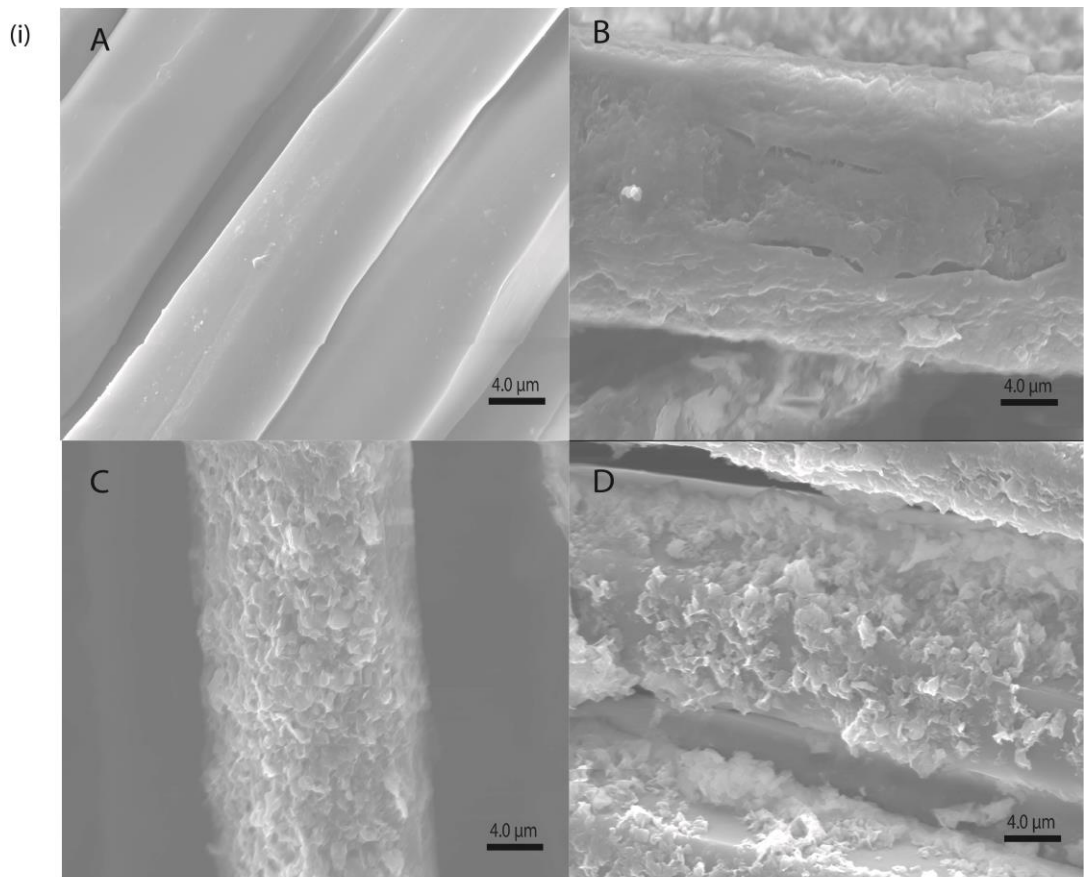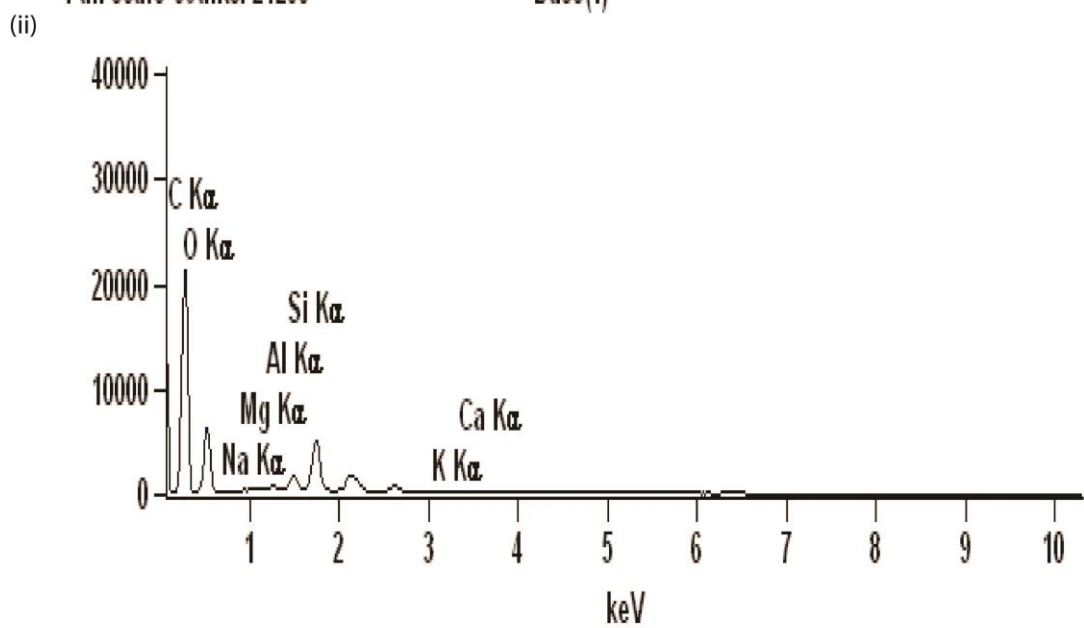
Figure 4.24: (i) SEM images of (A) pristine polyester, (B) and (C) BNC functionalized polyester, and (D) washed BNC functionalized polyester, and (ii) EDX spectrum of BNC functionalized polyester

4.12   Wash fastness property and abrasion resistance

Withstanding ability of BNC on polyester fabrics was studied against washing and rubbing.

4.12.1 Wash fastness property

The wash fastness of fabrics was assessed according to the standard AATCC 61 (2A) method. The concentration of aluminium in fresh samples and washed samples, after 5 and 10 washing cycles, were determined using ICP-MS as explained in Sub-section 3.12.1. Table 4.3 and Figure 4.25 compare graphically the Al concentrations in BNC coated fresh polyester fabric samples against 5 and 10 times washed samples. After 5 washes, it was observed that 1.02 mg and 1.15 mg of Al have leached out to water from 1 mmoldm^{-3} and 2 mmoldm^{-3} APTES modified polyester, respectively. This is due to BNC on top of the fabric surface, which are bound physically or with weak forces. As discussed in Chapter 2 and Figure 4.26 (a), hydroxyl groups of BNC initially bind with silanol groups of APTES via H-bonds, and then form strong covalent siloxane bonds on heating. If the siloxane bond is absent and BNC is bound with APTES only via H-bonds, it is very difficult to withstand for washing (Figure 4.26 (b), (c) and (d)). Further, some APTES molecules which are not bound to fibre, but bound with APTES network through siloxane bonds, have their amino groups free. These free amino groups could bind through H-bonds with hydroxyl groups of BNC (Figure 4.26 (e)). These bonds were poor against several washes. Further, smaller size BNC is trapped in the gaps of fibres of fabrics and in the cavities of APTES network. Hence, these result in leaching of loosely bound BNC to water. However, after 10 washes, it was clearly evident from the Table 4.3 that leaching out of Al was considerably low. After removal of physically bound BNC, covalently attached BNC has a strong ability to withstand for several washes. This confirms the presence of strong covalent bond between the fabric and the coating. In fact, the siloxane bond between APTES and BNC, and the amide bond between BNC and polyester fabric, have given the best adhesion and washing resistance properties to

the treated polyester fabric. These results proved that washing is not a barrier to moisture management property in long term using of BNC coated fabrics.

Table 4.3: Amount of Al contains in BNC grafted APTES modified polyester fabric samples

Al content in	BNC grafted on 1 mmoldm^{-3} APTES modified polyester	BNC grafted on 2 mmoldm^{-3} APTES modified polyester
Original fabric	9.53 mg	12.36 mg
Fabric sample after 5 washes	8.51 mg	11.21 mg
Fabric sample after10 washes	8.20 mg	11.04 mg
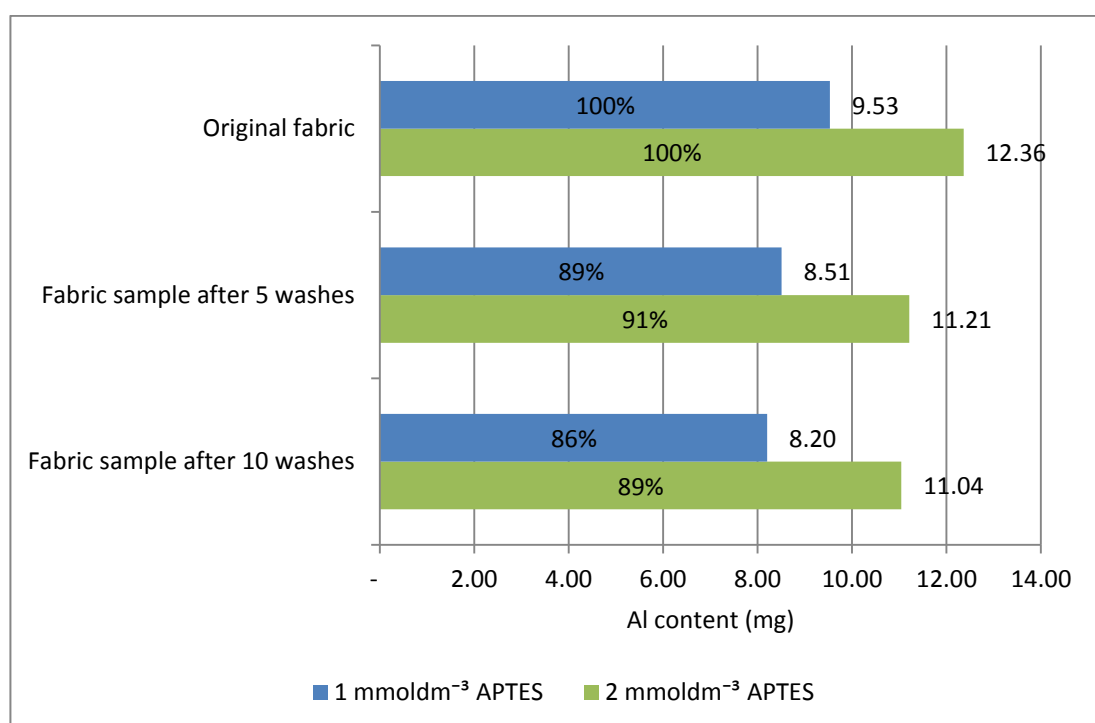
Figure 4.25: Amount of Al contains in BNC grafted APTES modified polyester fabric samples
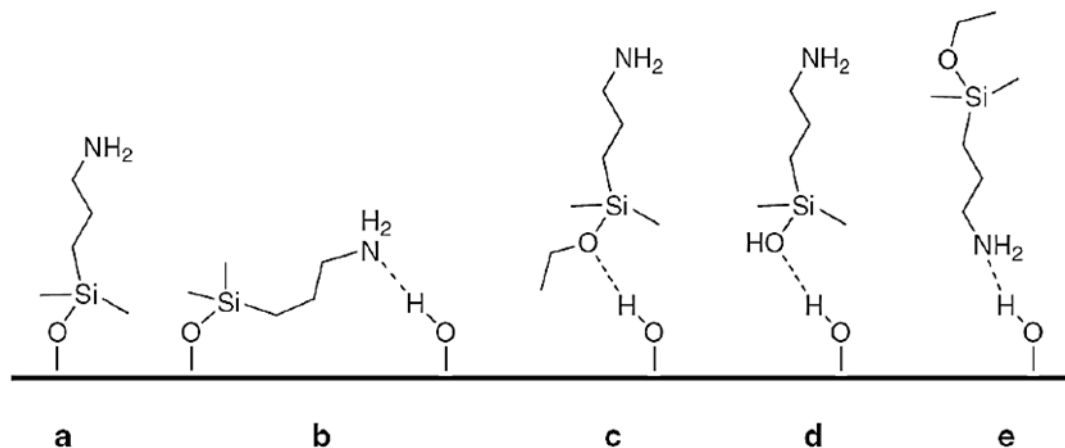
Figure 4.26: Possible different bonding types between BNC and APTES

4.12.2 Abrasion resistance

The stability of grafting of BNC was tested against abrasion according to the AATCC 08 method as discussed in Sub-section 3.12.2. An abrasion resistance tester was used to measure the abrasion fastness of BNC on polyester fabrics. The amount of Al on abraded cloth after 5000 cycles of rubbing was measured using XRF elemental analysis. Table 4.4 compares the Al atomic percentage in abraded cloth before and after abrasion with BNC grafted fabrics. After the abrasion, Si content in standard abrasive cloth has risen slightly, while Al content remained negligible. These data proved that physically bound BNC has moved to the abrasive cloth, though the amount is not significant. Figure 4.27 shows a deformation fibre in the abraded BNC grafted fabric, with no noticeable damages to BNC coating on fibres. Owing to strong covalent bond network of BNC and APTES with polyester fabric, BNC grafted fabrics were able to withstand 5000 abrasion cycles with negligible damage to the coating.

Table 4.4: Si and Al atomic percentages of abraded cloth before and after abrasion with samples

Fabric sample	Si atomic %	Al atomic %
Standard abraded cloth before abrasion	1.23	0.00
Standard abraded cloth with 1 mmoldm^{-3} APTES after abrasion	1.77	0.00
Standard abraded cloth with 2 mmoldm^{-3} APTES after abrasion	1.45	0.00
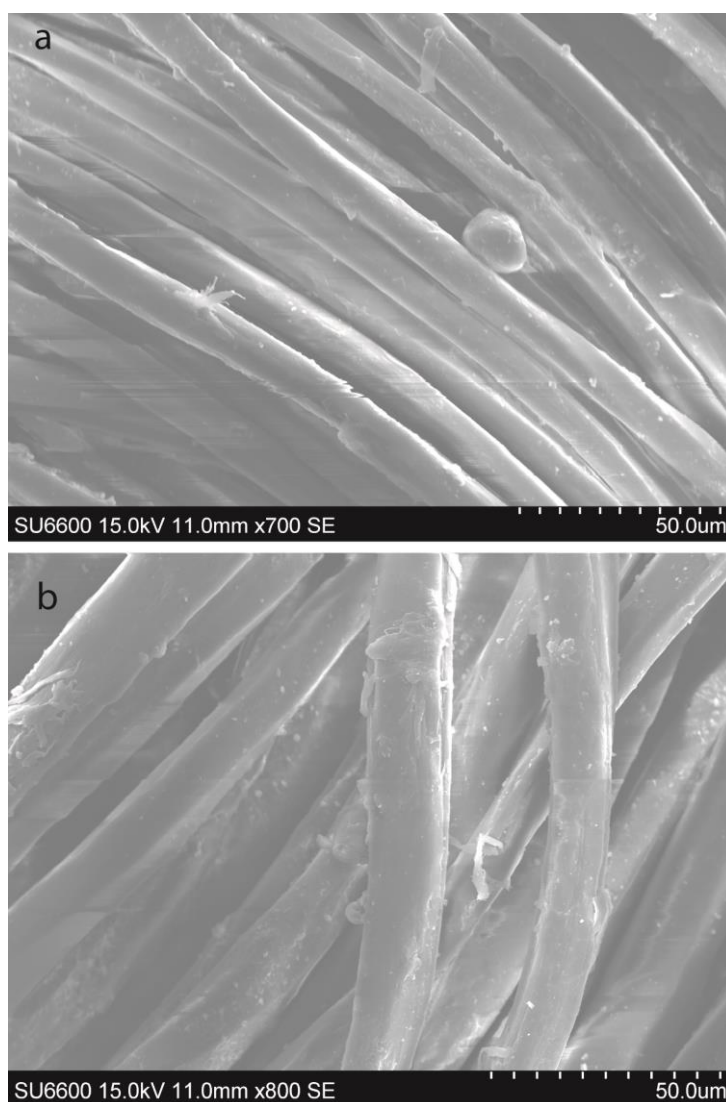
Figure 4.27: SEM images of (a) BNC grafted polyester, and (b) same fabric after abrasion

4.13 Optimization of parameters

This section mainly looks into optimizing conditions for the reaction of APTES and polyester fabric. There are three factors which affect this reaction, which are solvent, temperature, and concentration of APTES. However, the solvent and temperature were kept fixed while changing the concentration of APTES in the studies relevant to this section. The successfulness, economical feasibility and sustainability of the research depend on its ability to move from laboratory to industrial scale. Therefore, most of the processes in industries are being done in water medium. Further, use of other solvents such as organic solvents may hinder the hydrophilicity of BNC due to intercalation of BNC with organic molecules, which leads BNC to hydrophobicity.

Temperature for this reaction was kept constant at 80 ℃ according to the literature, since most of the modifications for polyester such as dyeing are being done at higher temperatures [93]. Polyester fabrics are dyed using disperse dye at near to polyester glass transition temperature. Further, the dormant nature of polyester limits reaction of dye molecules with fibres, and therefore diffusing them into the fibres. Similarly, high temperature was an advantage to diffuse APTES molecules into the fibres in this reaction.

Concentration of APTES was kept at low as described in Section 4.4. The uncondensed monomer silanol is a considerably small molecule, which can diffuse into fibres effortlessly. If not, it is a challenge for oligomers (condensed lager molecules of silanol) of APTES to diffuse into fibres.

4.14 Optimization of concentration of APTES on BNC loading

Binding of BNC at four different concentrations of APTES was analysed using TGA and XRF.

4.14.1 TGA

A comparison of ash content in each APTES modified fabric and BNC grafted fabric are shown in Figure 4.28, Figure 4.29, Figure 4.30 and Figure 4.31. Weight gains of APTES modified fabric over pristine polyester, and BNC grafted fabric over APTES modified polyester, are illustrated in Table 4.5. When increasing the concentration of APTES, the weight of ash content has also gone up. This pattern indicates that loading of APTES on fabrics has increased along with its concentration. This can be further explained as APTES initially reacts with polyester fibres, and if more APTES molecules are present in the reaction mixture, it starts to form multilayers of APTES via self-condensation (Figure 4.32). However, when increasing the APTES concentration, a different pattern was observed in loading of BNC. This is owing to the low concentration of APTES not encouraging formation of multilayers (self-condensation). Lack of APTES in reaction mixture encourages more freely available silanol groups to react with BNC. In contrast, self-condensation occurs at high concentrations of APTES, which leaves less silanols to react with BNC. Consequently, low loading of BNC was observed as increasing the concentration of APTES. When increasing the concentration of APTES, BNC loading also increased up to a certain concentration and then started to decrease.
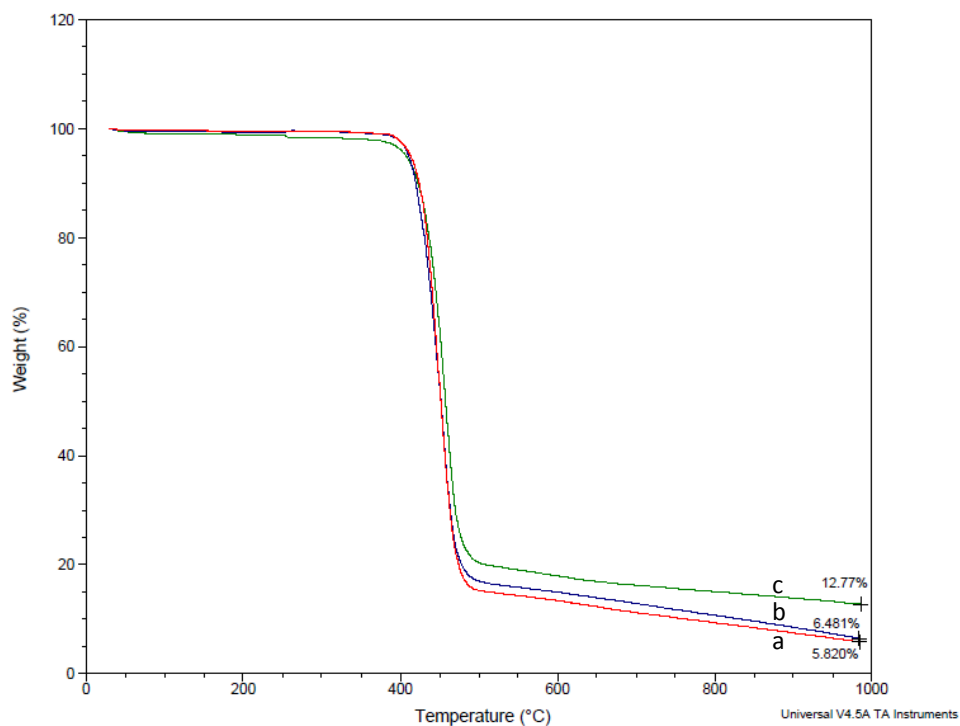
Figure 4.28: Thermograms of (a) pristine polyester, (b) 1 mmoldm^{-3} APTES modified polyester, and (c) BNC grafted on 1 mmoldm^{-3} APTES modified polyester
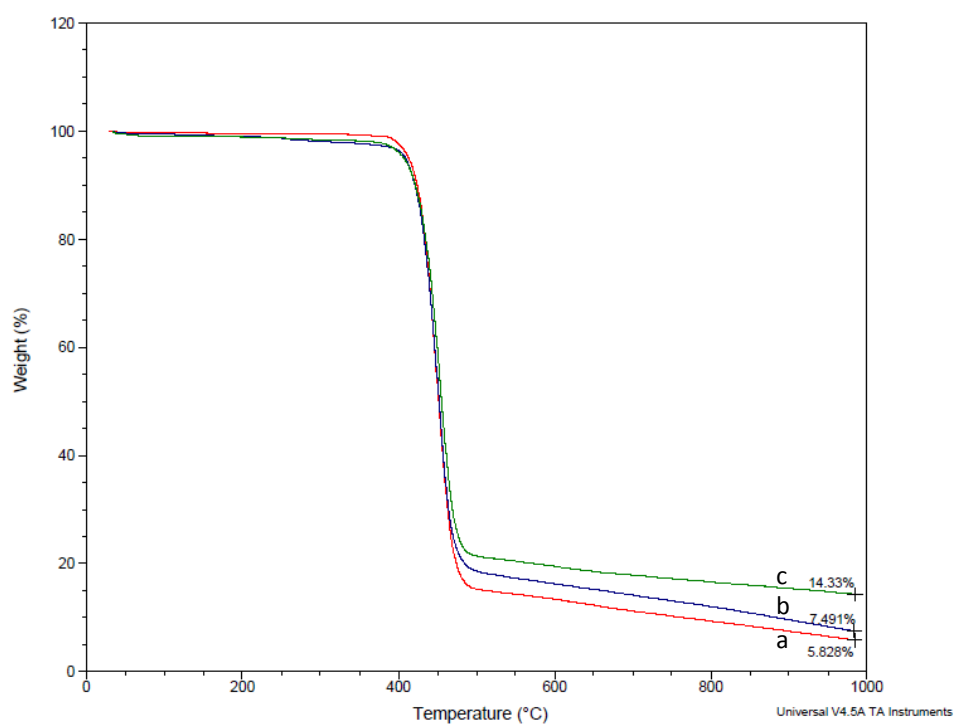
Figure 4.29: Thermograms of (a) pristine polyester, (b) 2 mmoldm^{-3} APTES modified polyester, and (c) BNC grafted on 2 mmoldm^{-3} APTES modified polyester
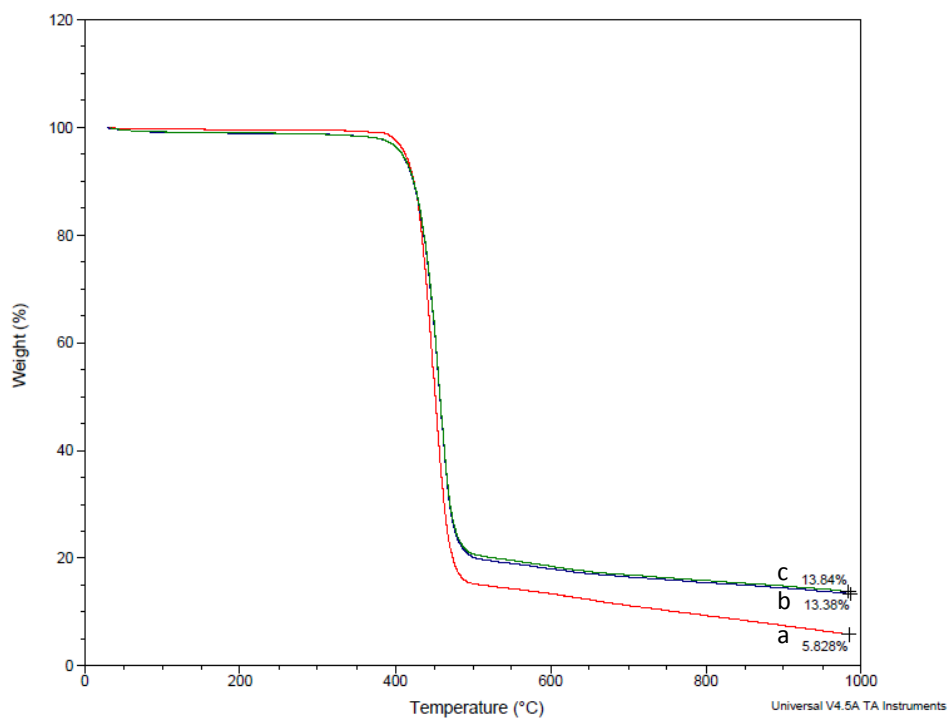
Figure 4.30: Thermograms of (a) pristine polyester, (b) 3 mmoldm^{-3} APTES modified polyester, and (c) BNC grafted on 3 mmoldm^{-3} APTES modified polyester
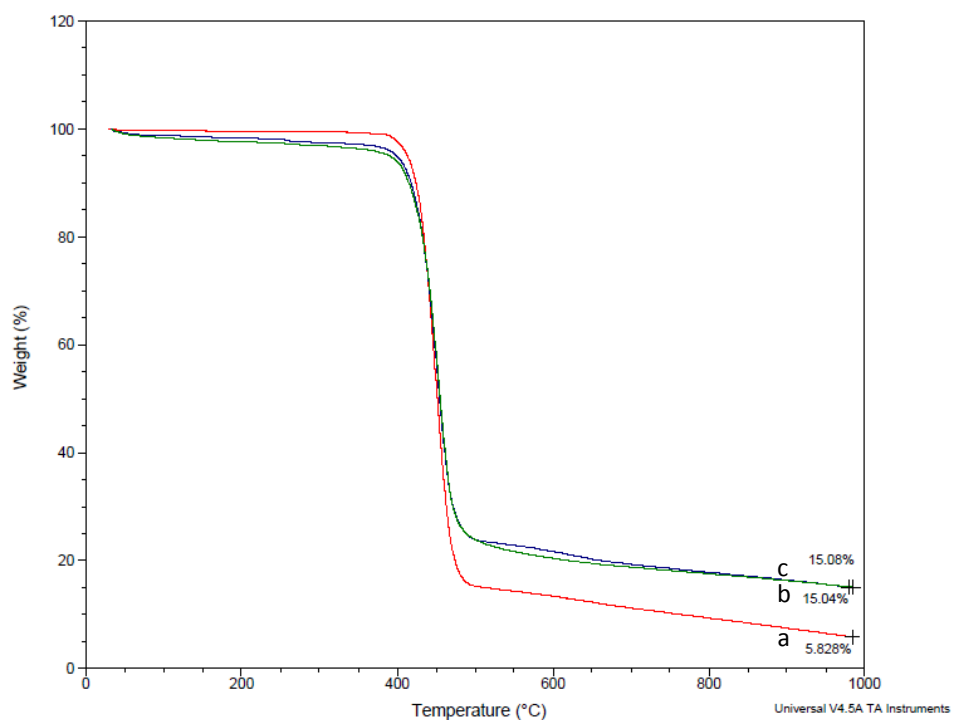
Figure 4.31: Thermograms of (a) pristine polyester, (b) 4 mmoldm^{-3} APTES modified polyester, and (c) BNC grafted on 4 mmoldm^{-3} APTES modified polyester

Table 4.5: Mean weight gain of APTES and BNC modified polyester fabric samples

Fabric sample	Mean weight gain % (over pristine polyester)	Mean weight gain % (over APTES modified polyester)
1 mmoldm^{-3} APTES modified polyester	0.66	
2 mmoldm^{-3} APTES modified polyester	1.68	
3 mmoldm^{-3} APTES modified polyester	7.50	
4 mmoldm^{-3} APTES modified polyester	9.17	
BNC grafted on 1 mmoldm^{-3} APTES modified polyester		6.30
BNC grafted on 2 mmoldm^{-3} APTES modified polyester		6.83
BNC grafted on 3 mmoldm^{-3} APTES modified polyester		1.65
BNC grafted on 4 mmoldm^{-3} APTES modified polyester		0.05
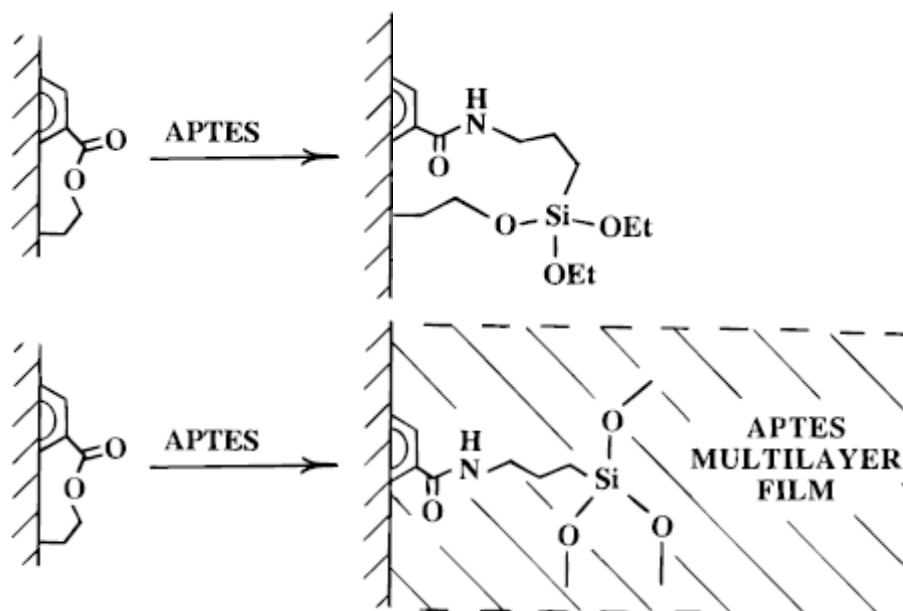
Figure 4.32: Reaction between APTES and polyester leading to multilayer formation [93]

4.14.2 XRF

The XRF Si atomic percentage of APTES modified fabrics, and Si and Al atomic percentages of BNC grafted fabrics are shown in Table 4.6 and Table 4.7, respectively. XRF data proved that Si atomic percentage also increases when increasing the concentration of APTES.

Table 4.6: Si atomic percentage of APTES modified polyester fabric samples

Fabric sample	Si atomic %
Pristine polyester	2.65
1 mmoldm^{-3} APTES modified polyester	23.58
2 mmoldm^{-3} APTES modified polyester	24.45
3 mmoldm^{-3} APTES modified polyester	28.48
4 mmoldm^{-3} APTES modified polyester	30.53

XRF data proved that Al atomic percentage also increases when increasing the concentration of APTES up to 2 mmoldm^{-3}. Thereafter, the Al atomic percentage started decreasing with increased APTES concentrations. This Al exists only in BNC. It was observed that binding of BNC on APTES modified fabrics is not favourable at high concentrations of APTES. When total APTES molecules are more than required to cover the surface of fabric, it starts to form a network consists of multilayers of APTES. Hence, self-condensation of APTES reduced its hydroxyl groups available to react with hydroxyl groups of BNC. Consequently, less BNC loading on fabrics was observed.

Table 4.7: Si and Al atomic percentages of BNC modified polyester fabric samples

Fabric sample	Si atomic %	Al atomic %
BNC grafted on 1 mmoldm^{-3} APTES modified polyester	24.06	4.80
BNC grafted on 2 mmoldm^{-3} APTES modified polyester	25.43	6.36
BNC grafted on 3 mmoldm^{-3} APTES modified polyester	28.30	4.40
BNC grafted on 4 mmoldm^{-3} APTES modified polyester	30.01	0.00

4.15   Moisture management testing

The moisture management properties such as drop test, absorptive capacity, drying rate and vertical wicking (warp and weft) of pristine polyester, BNC grafted APTES modified polyester and washed fabrics are depicted in Table 4.8.

4.15.1 Drop test

Figure 4.33 shows a comparison of wetting times of fabric samples, obtained in absorbency drop test. Since there are no water bonding groups on pristine polyester fabric, water drops just stay on the fabric without being absorbed. However, with the time, water molecules go into the free spaces in fibres very slowly. Therefore, it takes more time to absorb water. However, after treating with BNC, the wetting time has drastically gone down due to superior water absorbing properties of BNC, such as hydroxyl groups and high swelling capacity. If the test values are analysed further, it can be seen that wetting time decreases when increasing the APTES concentration up to 2 mmoldm^{-3}. From 3 mmoldm^{-3} onwards, the wetting time started increasing with increased APTES concentrations. This behaviour can be clearly explained using the concentration of BNC on polyester fabrics. As discussed in Sub-section 4.14.1 and Sub-section 4.14.2, when increasing the concentration of APTES, multilayers of APTES (water insoluble resinous oligomers and polymers) were formed on the fabric due to rapid self-condensation of silanol [74, 93]. This results in absence of silanol groups on the fabric surface to bind with BNC. Consequently, the limited silanol groups facilitated the bonding with BNC. Therefore, this implies that amount of BNC on polyester directly affects the wetting time of BNC coated fabrics. Hydroxyl groups on BNC and nanospace of BNC attracted more water molecules, which decreased the wetting time. Most of fibres were well coated with BNC, which facilitated water to travel over the surface very rapidly. After 10 washes, due to the removal of physically bound BNC, wetting time has increased slightly.

Table 4.8: Results of moisture management properties of pristine polyester, BNC grafted APTES modified polyester and washed fabrics

Fabric sample		Wetting time (sec)	Absorptive capacity (%)	Drying rate (ml/h)	Vertical wicking length (warp) (cm)			Vertical wicking length (weft) (cm)		
					2 min	5 min	10 min	2 min	5 min	10 min
Pristine polyester		12.10	51	0.17	2.0	3.0	4.0	1.0	2.0	3.0
BNC grafted on 1 mmoldm^{-3} APTES modified polyester	Original	0.93	202	0.34	7.0	9.0	10.7	4.2	6.4	7.4
	Washed	0.90	197	0.33	7.0	9.0	10.5	4.2	6.4	7.0
BNC grafted on 2 mmoldm^{-3} APTES modified polyester	Original	0.87	220	0.38	7.5	9.5	11.0	4.5	6.5	8.0
	Washed	0.82	210	0.37	7.5	9.3	10.8	4.5	6.4	7.9
BNC grafted on 3 mmoldm^{-3} APTES modified polyester	Original	1.04	184	0.27	6.5	8.5	10.4	4.0	6.0	7.0
	Washed	1.13	168	0.27	6.5	8.5	10.0	4.0	5.6	6.8
BNC grafted on 4 mmoldm^{-3} APTES modified polyester	Original	4.12	120	0.20	4.8	5.4	6.0	3.0	3.8	4.5
	Washed	4.10	114	0.20	4.0	5.0	5.5	3.0	3.7	4.0
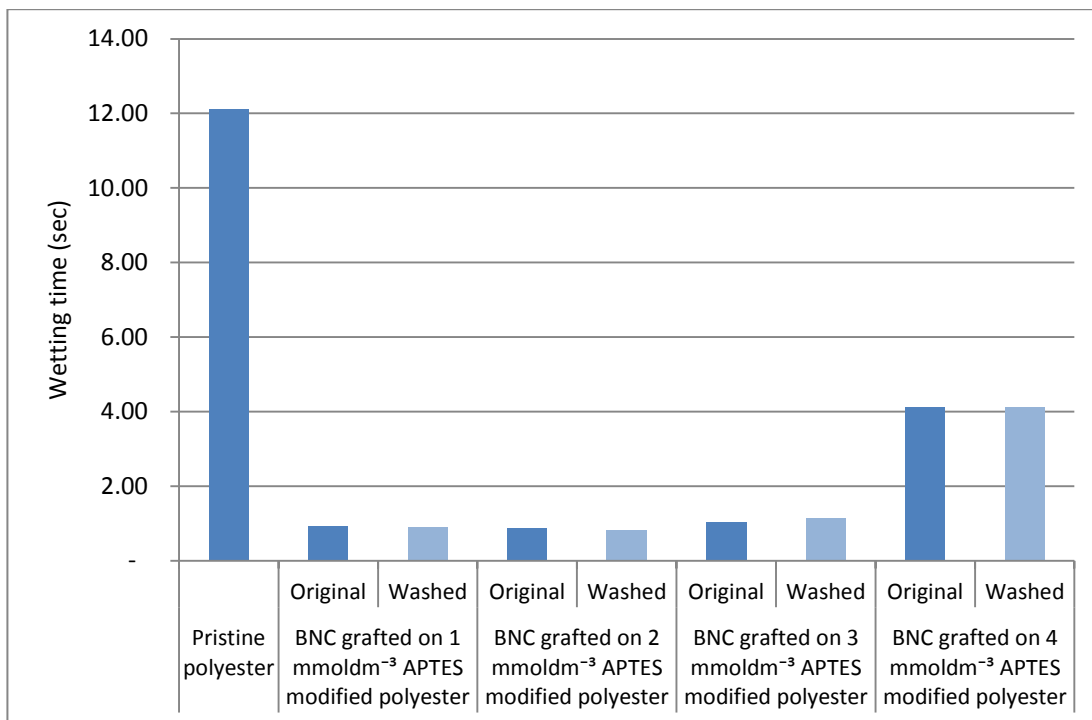
Figure 4.33: Wetting time of pristine fabric, BNC grafted APTES modified polyester and washed fabrics

In Figure 4.34, a drop of water was dropped on pristine and BNC grafted polyester to demonstrate the superior wettability of modified polyester. An Infra-red (IR) image (Figure 4.34 (B)) was taken to clearly demonstrate the spreading of a water drop on BNC grafted polyester. Hydrophilic nature of BNC attracts water while its excellent swelling capacity enhances spreading of water, promoting the superior wettability of BNC grafted fabric. Moreover, due to nano size of clay, there is an abundance of broken edges of clay, rich with hydroxyl groups sticking out present on the fabric, which provide excellent sites for water to cling immediately.
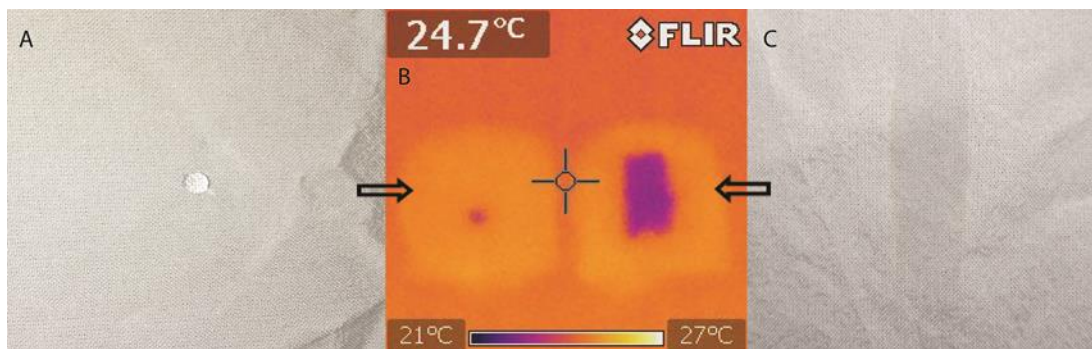
Figure 4.34: Immediate view of a water drop fallen on (A) pristine polyester, and (C) BNC functionalized polyester, and (B) images (A) and (C) through IR camera

4.15.2 Absorptive capacity

Absorptive capacity of a fabric indicates the amount of water absorbed by the fabric sample. According to Figure 4.35, absorptive capacity of pristine polyester is low compared to modified fabrics due to its hydrophobicity. The absorptive capacity is excellent after the BNC treatment. However, as discussed in Sub-section 4.15.1, high concentration of APTES on fabric reduced the amount of BNC on the fabric. More BNC on fabric increased the absorption of water. Hydroxyl groups on BNC edges helped to adsorb water molecules, while absorbing more and more water into expandable interlayers. Porosity nature of BNC assists water molecules to travel at a higher speed. This results in high capacity of absorbing water.
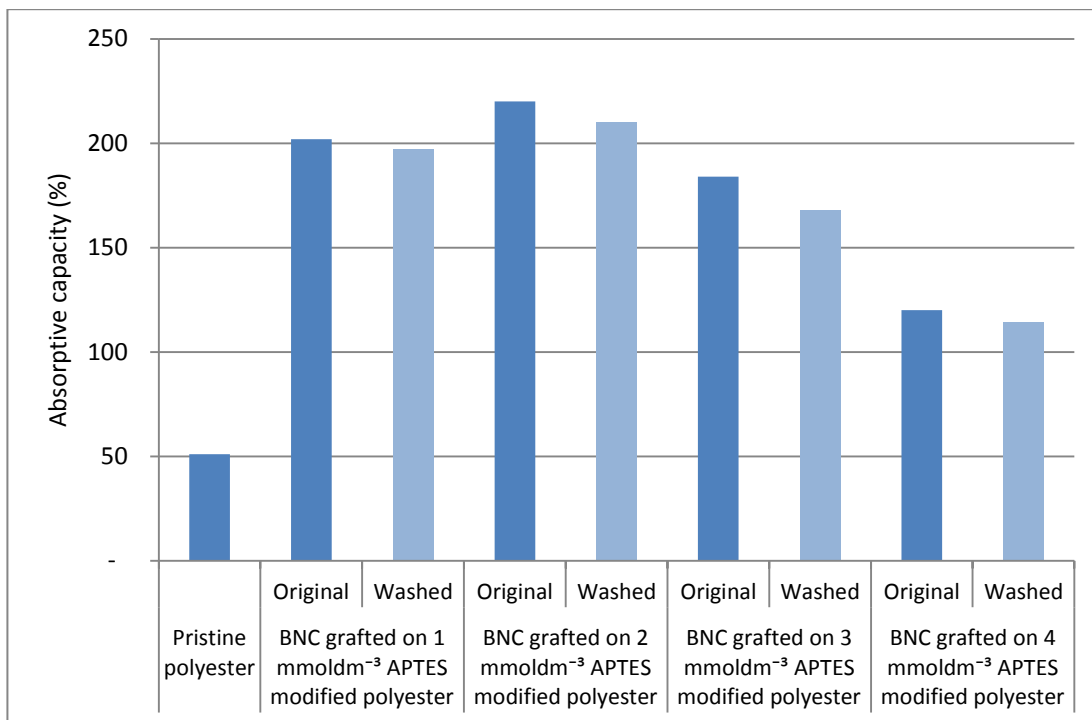
Figure 4.35: Absorptive capacity of pristine fabric, BNC grafted APTES modified polyester and washed fabrics

4.15.3 Drying rate

Figure 4.36 shows the testing set up of measuring drying rate of fabric sample, and how the fabric sample appeared through IR camera before and after adding a water drop. As shown in Figure 4.34, the wetted area was considerably low in pristine polyester fabric, as its hydrophobic nature restricted the water flow. However, BNC coated fabrics had a higher speed of water absorption, which helped water being spread in a larger area. Fibres of BNC grafted polyester fabric were fully covered by BNC, and its porosity nature further assisted to spread water at a higher speed to achieve a larger wetted area. Therefore, these results show a better drying behaviour. Figure 4.37 depicts the comparative results of drying rate of fabric samples. The moisture gradient between wetted and non-wetted areas was eliminated by the super hydrophilicity of BNC. Water spreading area and spreading speed are very important for drying. Spreading speed of a fabric indicates the ability of water to move on fabric's plane. A slow drying fabric has a small spreading area and spreading speed.

Pristine polyester fabric displayed this behaviour, since its spreading area and spreading speed are poor compared to other modified fabrics. Hence, pristine polyester took more time for drying. However, BNC grafted fabrics show a lager spreading area and spreading speed, which directly contribute to fast drying. Further, the content of BNC on fabric significantly contributes to its drying rate, where decreasing BNC content decreases the spreading area and spreading speed.
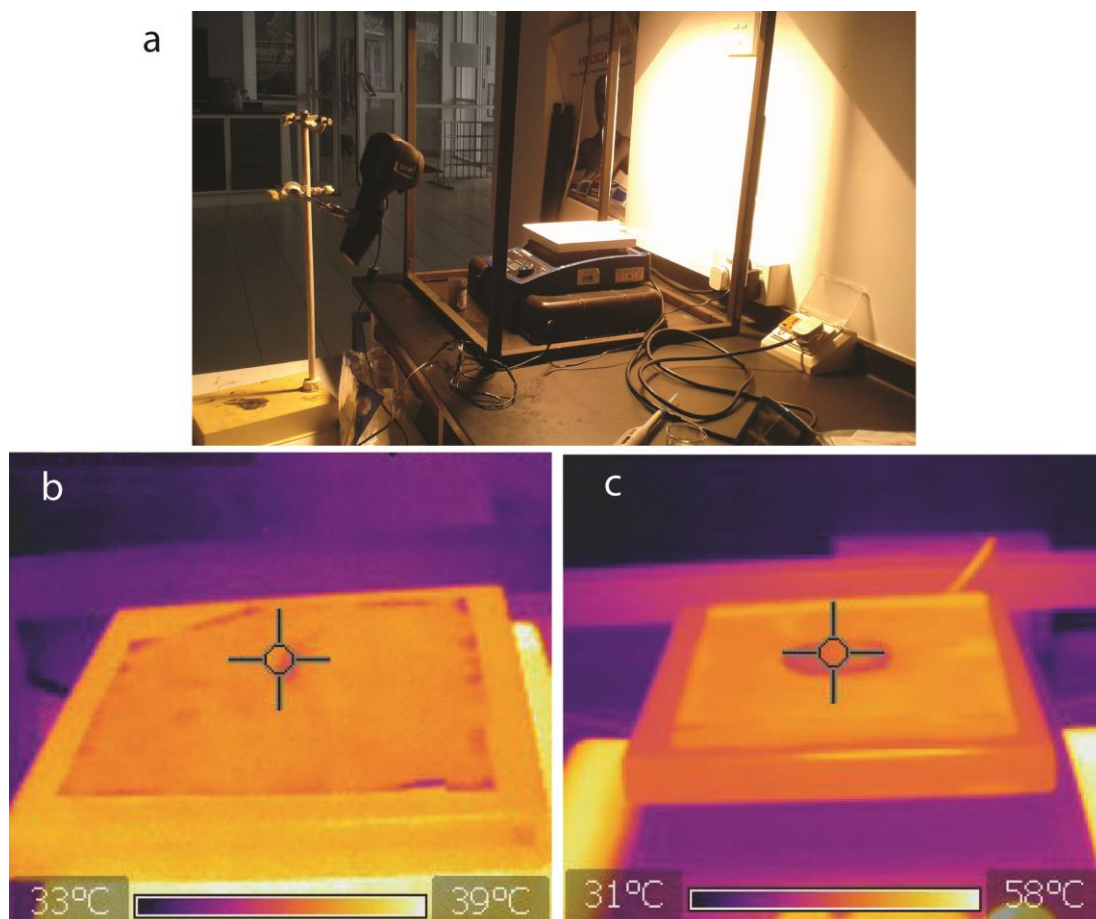
Figure 4.36: (a) Testing set up of measuring drying rate of fabric sample, (b) fabric sample through IR camera before adding a water drop, and (c) fabric sample through IR camera after adding a water drop
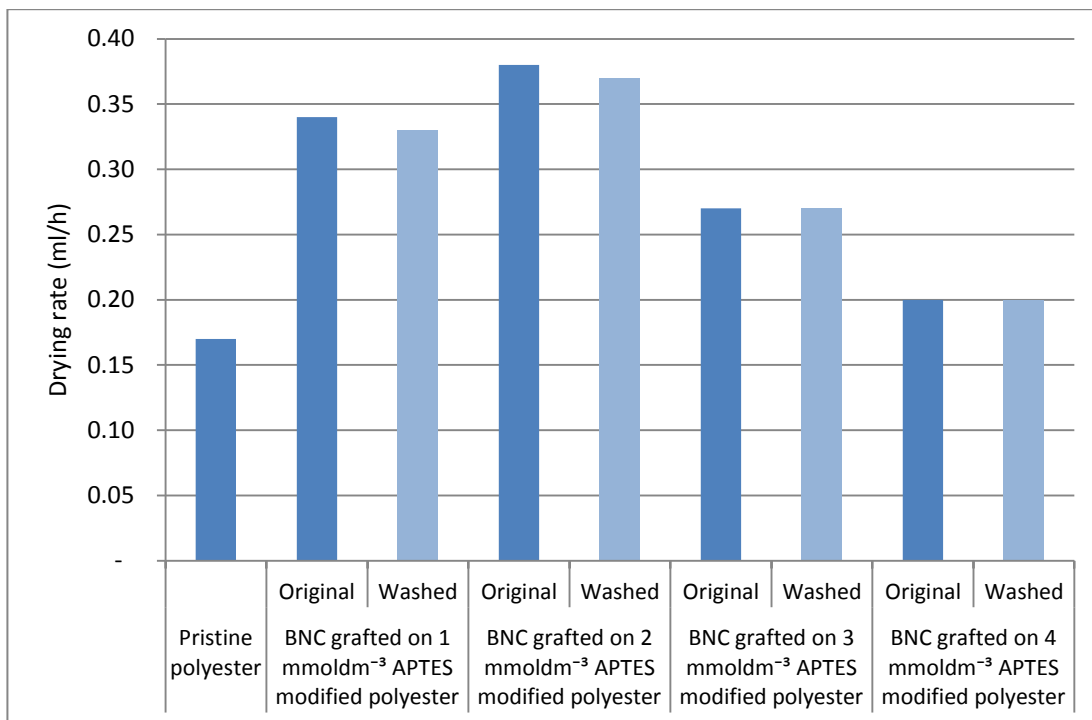
Figure 4.37: Drying rate of pristine fabric, BNC grafted APTES modified polyester and washed fabrics

4.15.4 Vertical wicking (warp and weft)

Wicking can be defined as the movement of any liquid along the capillary, which is present between fibres in yarn. When a strip of fabric is placed in a water container, the water wicking up the fabric is considered as vertical wicking. As discussed, pristine polyester doesn't have hydroxyl groups to pick up H_2O molecules. Hence, its wicking length is drastically low. However, after the modification, all fibres were covered by several layers of BNC, which had abundance of hydroxyl groups. These hydroxyl groups quickly bonded with water molecules, resulting in a higher length of wicking. Figure 4.38 shows IR images of uniformly wicked BNC grafted polyester fabrics, along with inconsistently wicked pristine polyester fabrics. In comparison to weft yarns, highly twisted warp yarns create an increased capillary action, resulting in a higher length of wicking. This increased wicking in warp direction is further facilitated by BNC in the modified fabric (Figure 4.39 and Figure 4.40).
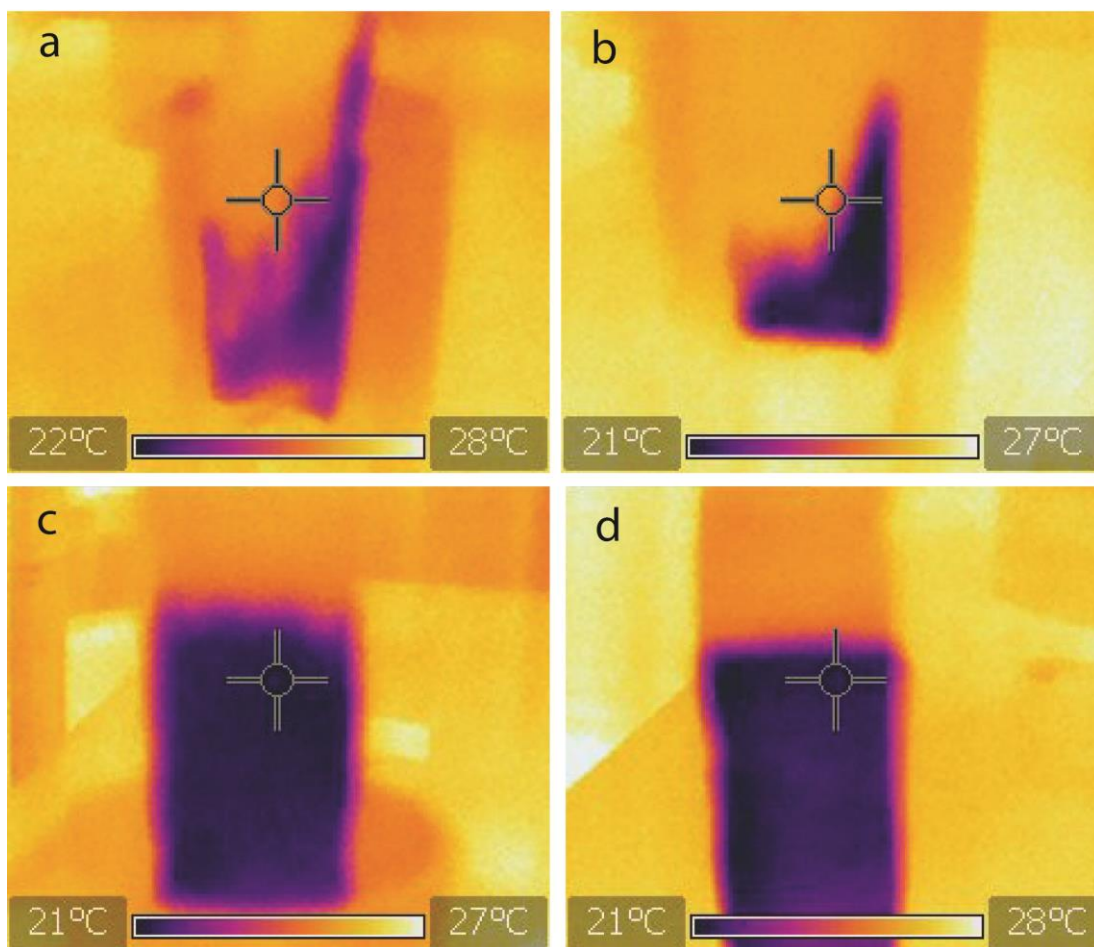
Figure 4.38: Vertical wicking images of (a) pristine polyester fabric (warp), (b) pristine polyester fabric (weft), (c) BNC coated polyester fabric (warp), and (d) BNC coated polyester fabric (weft)
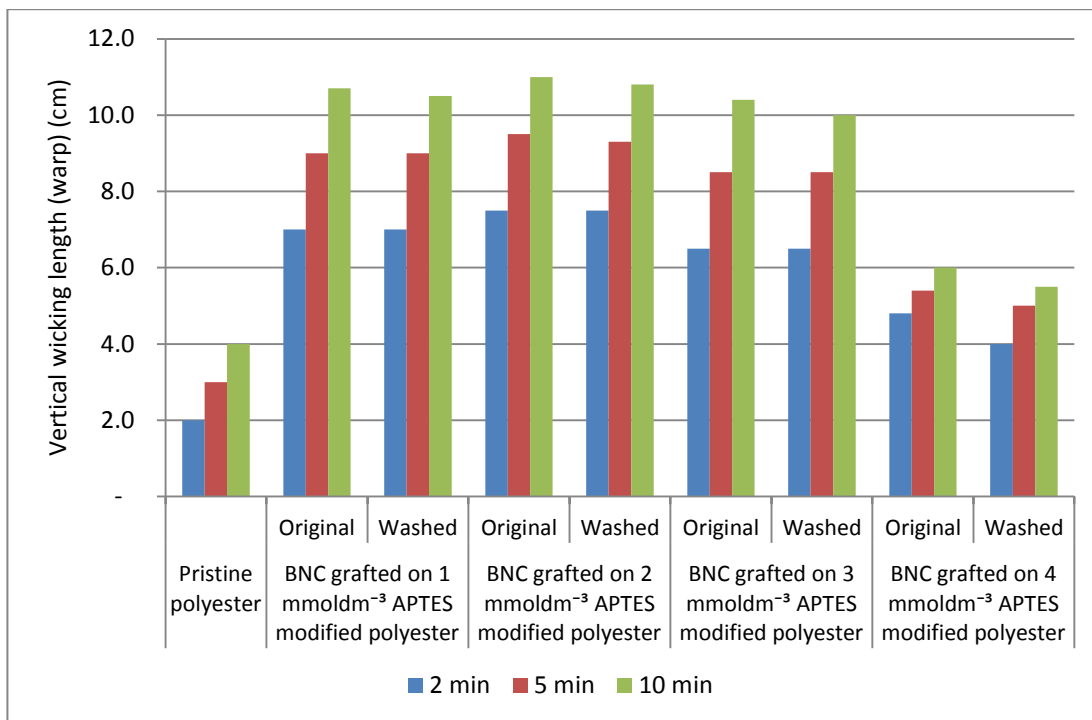
Figure 4.39: Vertical wicking length (warp) of pristine fabric, BNC grafted APTES modified polyester and washed fabrics
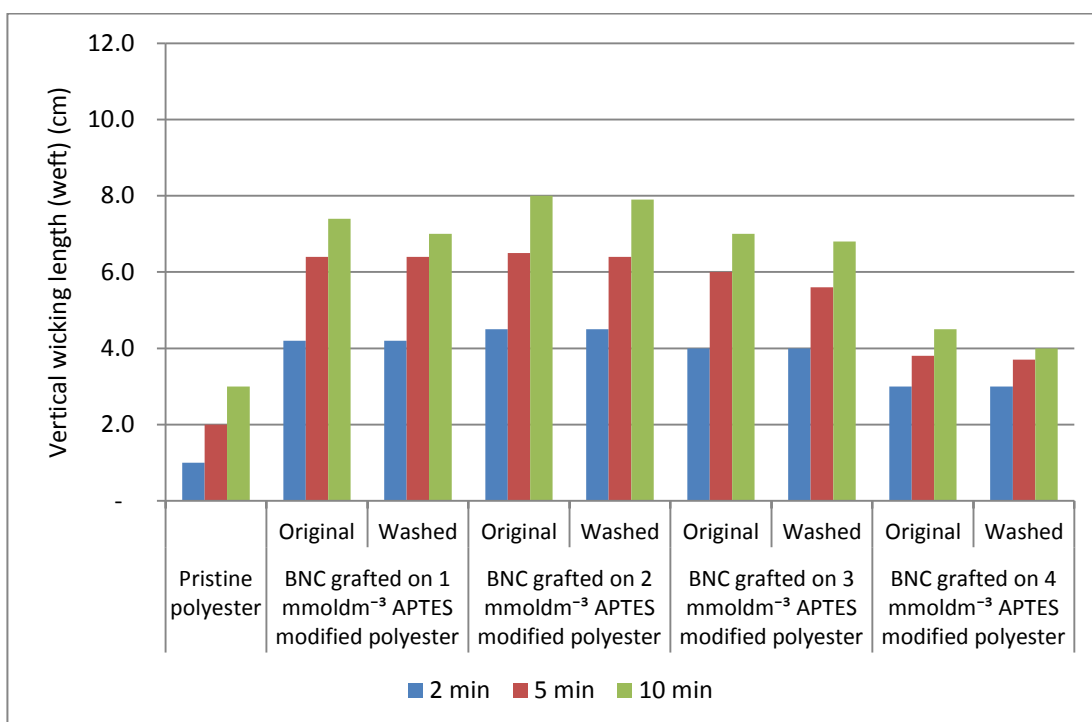
Figure 4.40: Vertical wicking length (weft) of pristine fabric, BNC grafted APTES modified polyester and washed fabrics

4.16 Physical properties and tensile strength of fabrics

Ultimately, the physical and mechanical properties of the modified fabric govern its end-use. These properties directly contribute to the comfortability and performance ability of fabrics. This section presents a set of physical and mechanical properties of BNC grafted 2 mmoldm^{-3} and 4 mmoldm^{-3} APTES modified polyester fabrics.

4.16.1 Weight and thickness

According to Table 4.9, after grafting with BNC, there is a slight weight gain and a slight increment in thickness in modified polyester fabrics.

Table 4.9: Weight and thickness of fabric samples

Fabric sample	Weight (g/m^2)	Thickness (mm)
Pristine polyester	70.84	2.0
BNC grafted on 2 mmoldm^{-3} APTES modified polyester	75.34	2.5
BNC grafted on 4 mmoldm^{-3} APTES modified polyester	75.58	2.5

4.16.2 Tensile strength

As a result of the chemical modification on pristine polyester fabric, the mechanical properties of the fabrics have changed. Thus, it is important to be aware of the fabric tensile strength and elongation properties of the modified fabric. In this study, many difficulties are involved particularly due to a great degree of strain variation during deformation. Table 4.10 shows the results of tensile strength test done on BNC grafted APTES modified polyester fabrics.

Table 4.10: Tensile strength of fabric samples

Fabric sample	Tensile strength (MPa)	
	Warp	Weft
Pristine polyester	3.36	3.07
BNC grafted on 2 mmoldm^{-3} APTES modified polyester	3.57	3.31
BNC grafted on 4 mmoldm^{-3} APTES modified polyester	3.54	3.27

As shown in Table 4.10, there is no significant change in the tensile strength of pristine polyester and BNC grafted polyester fabrics. However, the tensile strength of fabrics after modification has increased by 6.25% and 7.82% in warp and weft, respectively. This could be a result of BNC being grafted on each and every fibre. It has been reported that addition of silica and bentonite clay to fibres enhances the mechanical properties of fabrics such as tensile strength, elongation and tearing strength [81]. Hence, in this case, the network of APTES with BNC formed on fibres caused an improvement in elongation of the fibre (Table 4.11).

Table 4.11: Elongation of fabric samples

Fabric sample	Elongation at maximum force (%)	
	Warp	Weft
Pristine polyester	37.47	29.11
BNC grafted on 2 mmoldm^{-3} APTES modified polyester	41.57	29.85
BNC grafted on 4 mmoldm^{-3} APTES modified polyester	41.01	29.51

4.16.3 Air permeability

Air permeability of a fabric describes the degree to which a fabric is penetrable by air. Air flow occurs when air pressure is different on the two sides of the fabric. It is related to convective heat transfer by diffusion. The air permeability of pristine polyester and BNC grafted polyester are depicted in Table 4.12. Grafting of BNC has not significantly changed the air permeability of fabrics. Decrease in air permeability along with increased APTES concentrations signifies the contribution of APTES over BNC towards air permeability.

Table 4.12: Air permeability of fabric samples

Fabric sample	Air permeability (dm^3/s)
Pristine polyester	1.6801
BNC grafted on 2 mmoldm^{-3} APTES modified polyester	1.6373
BNC grafted on 4 mmoldm^{-3} APTES modified polyester	1.6369

4.16.4 Whiteness index

Whiteness index predicts the apparent degree of whiteness of a material based on tristimulus values determined according to one of the CIE standard methods, proposed by the CIE. After grafting BNC on polyester fabrics, the colour of polyester fabrics has changed to light pale yellow. This means that the fabrics have lost their original whiteness. Table 4.13 shows the values of CIE whiteness of fabric samples. The main colour adding agent for the fabrics is BNC, as APTES mostly tends to be white in colour. As discussed, when increasing concentration of APTES, BNC on fabrics started to decrease. Whiteness difference between pristine fabric and BNC grafted 2 mmoldm^{-3} APTES modified polyester is more than that of with BNC grafted 4 mmoldm^{-3} APTES modified polyester. This implies that higher BNC on polyester fabric changes the whiteness index more significantly.

Table 4.13: CIE whiteness of fabric samples

Fabric sample	M & S CIE whiteness
Pristine polyester	81.69
BNC grafted on 2 mmoldm^{-3} APTES modified polyester	69.90
BNC grafted on 4 mmoldm^{-3} APTES modified polyester	76.39

4.17   Summary

This chapter discussed the results, which were obtained in line with the methodology. Surface modification of polyester fabric was analysed quantitatively and qualitatively using results obtained from XPS, FTIR, XRD, SEM, TEM, XRF and TGA. Covalent bond formation of coupling agent with BNC and polyester fabric was proved using XPS and FTIR. 2 mmoldm^{-3} APTES was shown as the optimum concentration for highest BNC loading on polyester fabrics, which also showed the

best moisture management among the modified fabrics. Further, physical and mechanical properties of modified fabrics remained unchanged, while tensile strength and elongation showed slight improvement. Withstand ability against 10 washing cycles proved and validated the proposed modification.

5.   CONCLUSIONS AND RECOMMENDATIONS

5.1   Introduction

The main driving force for carrying out this research was to eliminate the hydrophobicity of polyester fabrics, while increasing their hydrophilicity, moisture transfer and evaporation. An extensive literature survey facilitated to identify the background of the study and the knowledge gap, which this research needed to address. Thus, after identifying the requirement of a modification for polyester, which is an industrially feasible and consumer benign method, BNC was applied on polyester fabrics.

5.2   Key conclusions

Surface modification of polyester fabric was analysed quantitatively and qualitatively using results obtained from XPS, FTIR, XRD, TGA, SEM and TEM. Covalent bond formation of coupling agent with BNC and polyester fabric was confirmed using XPS and FTIR. Peaks which are attributed to secondary amide were clearly observed in XPS and FTIR.

2 $mmoldm^{-3}$ APTES was shown as the optimum concentration for highest BNC loading on polyester fabrics, which also showed the best moisture management among the modified fabrics. Increasing the concentration of APTES led to more self-condensation of silanols, which hindered the reaction of BNC with APTES. Further, drop test, absorptive capacity, drying rate and wicking test results proved that moisture management property was majorly governed by the amount of BNC on the fabric.

Physically bound BNC removed during the initial washes. However, covalently attached BNC had a strong ability to withstand for 10 washing cycles and 5000 abrasion cycles. This confirmed the presence of strong covalent bonds between the

fabric and the coating. In fact, the siloxane bond between APTES and BNC, and the amide bond between BNC and polyester fabric, had given the best adhesion and washing resistance properties to the treated polyester fabric. These results proved that washing is not a barrier to moisture management property in long term using of BNC coated fabrics.

Physical and mechanical properties of modified fabrics remained unchanged, while tensile strength and elongation showed slight improvement. In contrast to the reported aminolysis reactions, the reaction of APTES with polyester fabric was free of degradation due to second reaction occurred between the alkoxide group created by the ester cleavage, and APTES. The alkoxide group created by the ester cleavage played an important role in the preservation of the polymeric structure. Hence, when analysing the results, extra strength had been gained by the polyester fibres after the modification.

Hence, this bio-inspired BNC coating on polyester appeared as a convenient green modification route to produce moisture management polyester fabric, which can be used for many hydrophilic fabric applications apart from its excellent ability to substitute expensive natural fibre usage in clothing.

5.3   Key recommendations

There are two main recommendations from this study.

A. This novel method for moisture management polyester fabric can be scaled up to industrial level.
B. Multifunctional fabrics or garments can be obtained by altering the desirable coupling agent and functional materials (further research).

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Appendix A: Publications on this study

A. S. B. Y. Abeywardena, S. Perera, P. V. T. Weerasinghe, K. M. N. D. Silva, S. Walpalage, M. C. W. Somaratne, N. M. Hettiarachchi, and S. Jeyasakthy, "Shape memory clay flaps assisted body cooling fabrics," *IOP Conference Series: Materials Science and Engineering*, vol. 459, p. 012027, Jul. 2018.

B. S. B.Y. Abeywardena, S. Perera, K. M. Nalin de Silva, S. Walpalage, M.C.W. Somaratne, "Localization of conductivity towards scalable and sustainable wearable electronics," *American Journal of Nanoscience & Nanotechnology Research*, vol. 6, no. 1,pp. 36-45, 2018.

C. S. Abeywardena, S. Perera, K. Silva, S. Walpalage, and M. Somaratne, "Bentonite Nanoclay Assisted Hydrophilic Nylon Fabrics," *Chemical Science International Journal*, vol. 23, no. 2, pp. 1–6, 2018.

D. S. B. Abeywardena, S. Perera, K. N. D. Silva, S. Walpalage, and M. Somaratne, "Mimicking elephant mud bathing to produce wettable polyester," *Materials Letters*, vol. 205, pp. 90–93, 2017.

E. S. B. Y. Abeywardena, S. Perera, K. M. N. D. Silva, and N. P. Tissera, "A facile method to modify bentonite nanoclay with silane," *International Nano Letters*, vol. 7, no. 3, pp. 237–241, 2017.

F. S. B.Y. Abeywardena, S. Perera, K.M. Nalin de Silva, S. Walpalage, "A bio-inspired approach to produce wettable nylon fabric," 4th International Conference on Nanoscience and Nanotechnology, Colombo, Sri Lanka, 2017.