Incorporation of Nanoparticles of Titanium Dioxide into Thermoplastic Textiles

A PhD thesis by

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Abstract

The incorporation of nanoparticles (NPs) into the surfaces of materials has received significant attention, especially in the area of textiles for self-cleaning. The sphericity and fast oxidation of metallic NPs when exposed to atmosphere are factors that can complicate incorporation into textile substrates. Using unique photocatalytic properties to decompose bacteria cells, NPs of titanium dioxide (TiO$_2$) are widely known as a common antimicrobial agent. The current research focuses on an innovative and novel coating process, where NPs of TiO$_2$ have been incorporated by embedding on single-side of a textile fabric surface, while retaining exposure of the NPs to photon sources. This technique was linked with the surface modification of textiles by thermal heating of the surface, which initiated the reduction of the fabrics elastic modulus by surface-softening, then embedding NPs into the heated zone of the textile surface. The NPs were sufficiently embedded for durable adherence to the fabric surface, while retaining an optimum exposure to photon sources. Thermoplastic textiles, with a viscoelastic stage, permit recovery of its surface when heated below its melting temperature, $T_m$ and were found to be an ideal material for this method of incorporation. The elastic modulus of polyethylene terephthalate (PET) textiles was investigated by thermodynamic experimental techniques, where the critical data was employed with two variant theories of contact mechanics. The study has found that embedding of NPs was better described by the JKR model due to its higher sensitivity to the reduction of the stiffness, the size of the NPs and the type of textile. Experimental rigs initiated the activation process for adherence of NPs to single-side of PET, cellulose acetate (CA) and acrylic thermoplastic polymer textiles. Analytical techniques, such as scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were employed to investigate the effective processing parameters of rigs. These properties included: quantitative and qualitative distribution of NPs on surfaces; durability of NPs to textiles; the textile transformation temperatures; and thermo-elastic responses. Film formation by agglomeration of NPs on textiles was noted where a higher concentration of TiO$_2$ was applied. A Pull-Off technique was employed for the measurement of durability of NPs to textiles presenting insufficient quantities of Ti on the adhesive-tapes for a conclusive outcome. Mapping by EDS techniques was a method of quantifying the surface coverage of NPs on PET, with inconclusive outcomes. A standardised laundering procedure applied to textiles was a method of testing the durability of NPs to textiles, where an AAS instruments was sued to quantify the content of TiO$_2$ ($\mu g/cm^2$). The best optimised textile of PET was achieved for 76% retention of TiO$_2$ between 1 and 40 laundering cycles. Empirical models were derived for the prediction of the optimum parameters for processing textiles by automatic rigs, and the prediction of TiO$_2$ ($\mu g/cm^2$) on PET. Automatic rigs were suitable to processing of thermoplastic textiles with NPs on single-side of its surface, and achieving increased retention where a reduction of the applied concentration and the higher surface heating was initiated. The outcomes of this study solve a major issue in the area of incorporation of NPs into textiles, by embedding NPs with high durability, and still exposing them for maximum antimicrobial abilities. The process has the potential for employment in the textile industry, for a cost effective method of preparing thermoplastic textiles providing efficient distribution and adherence of NPs on its surface, using inexpensive binding materials and processes.
Dedication

This thesis is dedicated to my loving partner Lisa, who has stood by my side with unquestionable support, understanding and encouragement. We are a team in this life of ours, and this journey would not have been possible without you.

My father, who is my hero, you have always been an inspiration and role model.

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My mother, who has been watching over me for too long, you are never far from my thoughts, I know I have made you proud. “He who laughs last laughs longest.”
Declaration

I, Patrick Cronin, hereby declare that the content of this thesis is a product of my own research. All sources of information employed as references and materials other than my own are duly acknowledged. This material has not been previously submitted to any University for any type of academic degree and has not been previously published.

Patrick Cronin
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List of Abbreviations

Symbols used in mathematical expressions:

\( A \)   Area
\( a \)   Contact Radius
\( c \)   Velocity of Light
\( \text{cm} \)   centimetre
\( d \)   Short dimension
\( E \)   Elastic modulus
\( E_g \)   Band-gap Energy
\( h \)   Planck's Constant
\( h_w \)   Lifshitz-van der Waals constant
\( l \)   liter
\( \text{mg} \)   milligram
\( \mu \text{g} \)   microgram
\( \text{MPa} \)   Mega Pascals
\( \text{mol} \)   mole
\( N \)   Newton
\( N \)   Cycles of laundering
\( P \)   Force
\( \text{ppm} \)   parts per million
\( R \)   Radius
\( \text{SA/V} \)   Surface Area to Volume
\( T \)   Temperature
\( T_g \)   Glass transition Temperature
\( T_m \)   Melting Temperature
\( t \)   time
\( W_a \)   Work of adhesion
\( \text{wt.\%} \)   Weight percentage
\( Y \)   Yield point
\( \dot{\lambda} \)   \((T_a - T_g)\)
\( \beta \)   \((T_m - T_g)\)
\( \gamma_s \)   Surface energy per unit area of a particular material
\( \Delta \)   Slope of A
\( \delta \)   Displacement
\( \varepsilon \)   Slope
\( Z \)   Separation distance
\( \lambda \)   Slope of B
\( \mu \)   JKR and DMT validation parameter
\( \eta \)   Molar number
\( \sigma \)   Stefan-Boltzmann Constant
\( \tau \)   Normalised temperature parameter
\( \nu \)   Poisson's ratio
\( \Omega \)   Concentration
**Other Acronyms:**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tr>
<td>AAS</td>
<td>Atomic Absorption Spectroscopy</td>
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<tr>
<td>AC</td>
<td>Alternating Current</td>
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<td>Silver</td>
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<td>American Society for Testing Materials</td>
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<td>Dynamic Mechanical Analysis</td>
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<tr>
<td>DMT</td>
<td>Derjaguin, Maugis and Tabor</td>
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<tr>
<td>EDX</td>
<td>Energy dispersive X-Ray Spectroscopy</td>
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<td>ENM</td>
<td>Engineered Nanomaterial</td>
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<tr>
<td>JKR</td>
<td>Johnson, Kendall and Roberts</td>
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<td><em>klebsiella pneumoniae</em></td>
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<td>Staphylococcus aureus</td>
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<td>V</td>
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<td>VR</td>
<td>Viscose Rayon</td>
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Publications

Journal Papers – Under Preparation


Patent Application/Invention Disclosures:


Buzalewicz, I., H. Podbielska, S.A.M Tofail, E. Dworniczek, R. Franiczek, M. Wawrzyńska, P. Cronin, P. Tiernan, “Illuminators for Photosterilization of Textiles with Nanoparticles”, Joint Invention Disclosure submitted to Wroclaw University of Technology, Poland, University of Limerick, Ireland and Wroclaw Medical University, Poland, September 2010.


Conference Presentations


1. Introduction

This thesis reports the outcome of an investigation of the assessed conditions of the adherence of nanoparticles (NPs) on a thermoplastic textile surface. At the foundation of this analysis, theoretical and experimental methods have been designed to examine conditions for the optimum adherence of NPs to the textile fibers surface. The choice of textile material was 100% polyethylene terephthalate (PET), which was an ideal thermoplastic material, with an even distribution of crystallinity and amorphous regions [1, 2]. The thermoplastic material permits the recovery of its physical properties after heating, where the limit of plastic deformation of the textile was not reached. The NPs of choice were sourced from commercially available titanium dioxide (TiO₂), which permitted easy dilution with water for optimisation of the concentration. NPs of TiO₂ (From here on termed TiO₂-NPs) are currently the most common photocatalytic material in nanotechnology [3].

The present chapter introduces the relevant research questions, the hypotheses and the methodological approach to this study. This chapter also highlights the gap within the literature that the current research fills, and then finally discusses the scope and organisation of the thesis.

1.1. Background

The incorporation of NPs onto the surface of a range of materials has received significant attention for the purpose of harnessing the extraordinary physicochemical properties of NPs into functional devices. Antimicrobial textiles that exploit the photocatalytic properties of certain oxide NPs such as TiO₂ and zinc oxide (ZnO) are being increasingly investigated for use in self-sterilising textiles. While TiO₂-NPs have long been known to have photocatalytic abilities [3], the incorporation of these NPs into a textile material remains a big challenge due to the sphericity and fast oxidation of metallic particles when exposed to atmosphere. There exists a need for the assessment and quantification of the adherence of NPs to surfaces in which they are incorporated. The toxicity of NPs is another reason for the
assessment of their adhesion to surfaces, especially in the area of human exposure and contact to free NPs dislodged or resulting from such surfaces [4, 5].

In addition, NPs must retain inherent photocatalytic abilities for antimicrobial application within the processed textile. Wearable textiles have another limitation when it comes to exploiting photocatalytic properties: only the outer surface of the textile is exposed to the sun or other photon sources. This means that NPs are only needed on single-side of the textile product, as having NPs on the inner side that is not exposed to the sun is practically meaningless and wasteful in terms of the surface content. It also increases the risk of dislodgement of NPs and is potentially hazardous for human health and environment. The NPs were to be efficiently distributed, where their unique surface area to volume (SA/V) property was utilised.

Textile fibres are made of either natural or synthetic polymers, or a blend of each, which does not readily bind with inorganic NPs. Currently NPs are incorporated in textiles using chemical binders. The problems associated with incorporating antimicrobial agents to textiles using binders, are the need for expensive binding agents, which also degrade with laundering and through general usage of the textile product. Chemical functionalisations of the textile surfaces or the surface of the NPs have been unsuccessful in improving the durability of these agents to textile surfaces. Such techniques are therefore ill-suited and unreliable for industrial textile applications, due to the increasing level of expense and environmental pollution they add.

Techniques commonly employed in the production of compound-based antimicrobial finishes of NPs or surface coatings on textiles yield a relatively thick, often continuous, two-sided coating on the surface. A continuous coating of antimicrobial agents on a textile surface is not, however, required for efficient photocatalytic activity from these NPs. Individual NPs with inherent photocatalytic abilities are known to exhibit efficient microbiocidal action before the colonisation of microbes [6]. Thicker and continuous coatings also result in a weaker interface between the textile and the NPs. This is because of the inherent difficulty in achieving a strong bond between the antimicrobial agent and the textile surface over a large area. A thick coating accentuates this problem by further weakening the
interface, due to the difference in elastic properties between harder metal-based antimicrobial agents and the soft and compliant textile matrix [7, 8]. Inefficient use of antimicrobial agents is a factor in the poor distribution of NPs over the potential surface area available for coating. Photocatalytic properties of antimicrobial agents have increased reactivity on the surface exposed to the stimulus which is responsible for the antimicrobial action.

The current research deals with these issues and intends to eliminate the problem of adherence between NPs and textile surfaces by employing a new method that exploits the thermoplastic nature of the textiles. The study has two broad objectives:

1. To apply photocatalytic NPs to a single-side of textiles made of thermoplastic polymer.
2. To assess and optimise the adherence and antimicrobial properties of these thermoplastic textiles incorporated with NPs.

1.2. Research Questions

With the preceding background, the current study investigates with the following research questions:

1. Will a reduced elastic modulus of thermoplastic textiles during embedding of NPs improve their adherence to the textile?
2. What is the most suitable treatment to permit efficient adherence of NPs to single-side of a thermoplastic textile surface?
3. Is it possible to embed NPs to thermoplastic textiles through softening of the textile surface by automatic rigs?
4. Will thermoplastic textiles prepared by embedding techniques with NPs have effective adherence during abrasive testing?
1.3. Research Hypotheses

The following hypotheses were used to find answers to the above research questions:

Hypothesis 1: The softening of thermoplastic textiles can be exploited to obtain a textile coated on single-side by strongly adherent NPs.

Hypothesis 2: The extent and strength of binding of these NPs will be related to the degree of softening.

Hypothesis 3: The distribution of NPs on the surface of the textile can be controlled by employing a coating process by spraying and varying its parameters.

1.4. Methodological Approach

The hypotheses outlined in the previous section, sets out three elements of investigation in the development of a thermoplastic textile incorporating NPs for antimicrobial properties: softening of textiles and control; application of pressure to enhance adhesion and durability; and controlled distribution of NPs using a spraying method. The first problem involved an investigation into a theoretical and an experimental approach to embedding of NPs to thermoplastic textiles. This methodology assessed a physical approach for increasing adherence of NPs to textile surfaces. On this basis, experimental rigs were implemented to soften the thermoplastic textiles by applying heat, and then pressing of NPs into the textile surfaces at this softened state. The second problem aimed to increase the compliance of the textile to the NPs that were embedded. This was achieved by varying the temperature of the textile surface during the embedding of the NPs, and then testing the durability of the NPs to the textile. An empirical relationship highlighted the importance of controlled softening of the thermoplastic textile surface during the embedding process. The third problem investigated the distribution and control of the NPs on the textile surface. The distribution and adherence NPs were efficiently controlled by applying an optimised applied concentration of spray before softening of the textile surface, where an empirical relationship was derived to examine the durability of NPs to textiles at varying concentrations.
The basic concept of incorporating NPs into a softened surface of thermoplastic textiles was proven manually on a laboratory scale. The success of incorporating such methodologies then led to a more efficient, automated, semi-industrial scale machine for incorporation of NPs. Figure 1.1 outlines this evolution in an experiment design that served two purposes:

1. The application of inorganic solid NPs to the substrate of single-side of a thermoplastic polymer textile for functionalization of photocatalytic properties.
2. The assessment and optimisation of the adherence of NPs and the efficiency of distribution to the thermoplastic textiles.

The advancement to the next step in the processes was decided on the foundation of each of the preceding steps as revealed by: theoretical considerations; surface distribution via scanning electron microscopy (SEM), energy dispersive X-ray (EDX), differential scanning calorimetry (DSC) measurements, dynamic mechanical analysis (DMA) measurements, atomic absorption spectroscopy (AAS), Pull-Off testing, and laundering by a domestic machine.
Figure 1.1 Flow diagram of methodology applied in the processing and optimisation of a thermoplastic polymeric textile embedded with NPs by manual hot-pressing (a), semi-automatic hot-pressing (b), and automatic hot-pressing (c).

The distribution of NPs on the textile surface was optimised by adjusting the concentration of NPs applied to the textile before the embedding stage. This concentration was delivered by a nozzle that finely disperses the solution of NPs. The quantity of NPs that were distributed by the spray-nozzle was limited by the rate of the fixed delivery output and spray pattern of the nozzle, where the distribution of NPs delivered was achieved by adjusting the rate at which the textile was fed under the spray. The thermal properties of the host textile material were examined before processing by embedding techniques, where they permitted the assessment of the
softened or viscoelastic region of the textile, and therefore highlighted the preferred parameter inputs of the embedding rigs. The viscoelastic region of a thermoplastic material allowed for plastic deformation of the material under an applied load [9]. The embedding techniques employed in this study utilise this region to adhere NPs by embedding them into the textile surface. This region of softening was achieved by lowering the elastic modulus of the thermoplastic textiles by increasing the surface temperature of the textile. A single-sided coating of NPs was achieved by applying the heat to single-side of the textile only, primarily the side that has been applied with NPs. The manual, semi- and automatic embedding techniques allowed for the optimisation of the concentration of NPs applied and the embedding temperature of textiles. An empirical model was then derived to understand the effect of the embedding rigs on the durability of NPs to textiles prepared with varying embedding temperatures and applied concentrations. The empirical model correlated with a high degree to the experimental data ($P > 0.05$). These models are limited by the fact they were derived for TiO$_2$-NPs embedded into PET textiles only.

NP embedding rigs were designed and constructed at the University of Limerick during the course of this study. The textile properties were assessed by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The morphology and surface characteristics of the modified textile surfaces were characterised by scanning electron microscopy (SEM) and energy dispersive X-Ray (EDS). A glue test, as per ASTM D4541-09 was employed to determine the durability of the bonding between TiO$_2$ and the polymer surface. Microbiology testing was conducted in collaboration with the clinical microbiologists of WMU. Members of WRUT constructed the UVA heating set-up unique to this study; see ‘Appendix A’ for microbiology results related to textile samples discussed in this study.

The embedding process and the strength of adhesion of NPs has been modelled based on a modification of contact mechanics theory, and will be discussed in Section 4.3. The contact radius was analysed as a function of the displacement of NPs into the textile surface. The effective load on NPs was assessed for a thermally activated PET textile surface, where the adhesion force between NPs and textile surface was also calculated. These interactions were examined for varying
temperature of the textile surface, or in this study, are termed active temperatures, $T_a$ where the surface permits increasing compliance of embedding. The $T_a$ permits the initiation of a viscoelastic region, where this action softens the surface of a thermoplastic textile, thereby reducing the elastic modulus of the surface. Mechanical and physical properties of NPs and textile surfaces were assessed by a combination of relevant literature survey, and experimental data.

1.5. Gap in the Literature that the Current Study Fulfils

Apart from the works discussed in Chapter 2, the author is not aware of any other research work detailing the adherence of TiO$_2$ NPs to thermoplastic textile surfaces. The main contribution from the author to the state of the art, involved the adherence of NPs to thermoplastic textiles using a novel heat treatment procedure [10], and conducting of embedding of NPs by hot-pressing techniques followed by extensive characterisation at each stage of processing. The research has developed quantitative techniques for the assessment of retention of NPs to PET, CA and acrylic textiles, by quantifying the TiO$_2$ content. This is a unique contribution to the state of the art, where TiO$_2$ retention was quantified by durability testing using cycles of laundering and analytical techniques.

Another important and unique contribution to the state of the art was to develop a theoretical understanding of displacement of NPs and the force required for their subsequent displacement into a thermoplastic textile surface. The reduction of the elastic modulus of the PET textile was utilised in contact mechanics theory, where the properties of both the textile and NPs were incorporated. The increasing compliance of PET textiles towards embedding of NPs at an increasing surface temperature of the textile was a significant outcome. The importance of controlling the elastic modulus of the textile by heat manipulation was highlighted by the theory.

This research also contributes to the state of the art by developing empirical models for the prediction of retention of TiO$_2$ NPs to PET textiles, either by quantifying the percentage, or the content of NPs present. The empirical models were developed from formulating the experimental data quantified through the application of the automatic embedding technique.
1.6. Scope of the Theses

The thesis was organised into eight Chapters and three Appendices.

Chapter One, ‘Introduction’ introduced the background and objectives of the study, research questions, hypothesis, methodology, advantages and limitations of the methodology. It provides details of the contribution that this study makes to the current state of the art, and also provides an outline of the organisation of the thesis.

Chapter Two, ‘Literature Review’ provided an overview of textile evolution, the modernisation of textiles for technical applications and current position in medical and healthcare environments. An overview of the mechanical properties of textiles was included, with a description of the barrier efficacy of polymeric materials. Properties and the biomedical and industrial applications of NPs in the form of engineered nanomaterials (ENM) were reviewed. The various techniques of producing an antimicrobial textile were also discussed in detail, including dip-coating, spin-coating and sonochemistry. Improvement methods of adherence of NPs to materials were discussed, followed by an overview of the potential toxicity they may exhibit. A detailed review of colloidal adhesion to surfaces was included, which focuses on theory relating to contacts between colloidal particles and material surfaces.

Chapter Three, ‘Methodology and Experimental Techniques’ detailed the analytical and processing techniques employed in this study. Theoretical considerations of surface contact of NPs with textiles were discussed. It also described the design and construction of the manual, semi-automatic and automatic embedding rigs employed processing techniques, and materials initialised with these rigs in this study. A Pull-Off test for the examination of the adherence of NPs to textiles was discussed in detail. Durability testing in the form of a domestic laundering standard was discussed as a technique of evaluating adherence of NPs to surfaces.

Chapter Four, ‘Nanoparticle Embedding to Thermoplastic Textiles: Theoretical Considerations’ described the analysis of the surface contact of TiO₂-NPs with thermoplastic PET textile surfaces. A detailed discussion on the effect of the elastic modulus of the PET, and its manipulation for increasing compliance with embedding of NPs was provided. Theories of contact mechanics were employed to investigate
the displacement of NPs on textile surfaces, the embedding force and the *Pull-Off* force required to remove NPs from the textile surface.

Chapter Five, ‘Nanoparticle Embedding to Thermoplastic Textiles: Experimental Results and Discussion’ described the outcomes of an experimental programme undertaken with the embedding rigs. A detailed discussion was presented on the optimum material and rig parameters for efficient distribution and adherence of NPs to the textile surfaces.

Chapter Six, ‘Nanoparticle Embedding to Thermoplastic Textiles: Empirical Model’ described an approach to derive a formula for the prediction of Retention of NPs to PET textiles. A model was also derived for the prediction of the optimum concentration of NPs and temperature of textile surface for embedding.

Chapter Seven, ‘Conclusions and Future Work’ described the final conclusions of the work to date, and outlined the future work that was planned and proposed.

Chapter Eight, ‘References’ listed all the references and sources consulted and reviewed in the present research project.

‘Appendix A’ provided the antimicrobial procedure and the results for textiles prepared in this study.

‘Appendix B’ provided drawings and schematics of embedding rigs.

‘Appendix C’ provided adhesive-tape results by EDS mapping.

‘Appendix D’ provided the derivation used to convert Ti (mg/l) quantified by AAS analytical techniques, to TiO₂ (µg/cm²) on a textile surface area.
2. Literature Review

This chapter provided an overview of textile materials incorporated with NPs employed as antimicrobial agents and the potential for application in health care environments. A detailed description of textile fabrics was provided, with the associated characteristics, properties and applications which permit popularity of this material in every aspect of modern life. The extensive employment of textiles in health care environments as a source of barrier resistance was discussed. This was followed by an investigation of the present and future applications associated with nanotechnology, more specifically in the area of NPs. The most popular NPs available to the market were detailed and described for potential applications and toxicity, with a brief introduction of the NPs with potential in the marketplace. The research and development of physical and chemical methods, processes and materials employed to instil microbiocidal properties into textile materials was investigated, with the most successful of those described in detail. Here the mechanisms that occur in surface coating, fibre extrusion and surface pre-treatment methods was discussed, with particular attention to the multiple variants that require optimisation. An investigation into the attraction and adhesion of organic and inorganic particles permitted on surfaces was presented, with specific focus on the area of contact mechanics. A theoretical and experimental review of sub-micron particle adhesion and deformation of surfaces was reviewed.

2.1. Textile Fundamentals

2.1.1. Common Terminologies and Characteristics of Textile Fibres
Textiles have a range of applications that can be categorised under clothing, furnishing and technical applications. Clothing and furnishing textiles are designed and manufactured from materials and processes where aesthetics and comfort towards the end user are the most desirable of attributes [11]. Technical textiles are designed towards gaining efficient performance of its physical properties so that it may fulfil the desired functions [12]. Functions include, but are not limited to:
mechanical, filtration, antibacterial and fungal, and protective functions from chemical and thermal attack.

Structures of textile fabrics can be separated into woven and non-woven categories. Non-woven fabrics are a combination of random fibres, held together through adhesive bonding, stitching or entanglement, as presented in Figure 2.1(a) [11]. Woven fabrics are manufactured, where yarns in the warp (lengthwise) direction pass under and over the weft (crosswise) yarns, as presented in Figure 2.1(b). The fibres form a series of lengths, where natural or synthetic materials are networked together to form a yarn, and then woven together to fabricate textile fabrics [13]. Woven fabrics are stiffer and less porous than non-woven fabrics, due to the tight weaving of fibres. The importance of both non-woven and woven textile fabrics in the medical industry is discussed in Section 2.1.2.

![Figure 2.1 Schematic illustration of fiber structure for nonwoven fabrics (a), and woven fabrics (b).](image_url)

The fiber size is expressed in terms of linear density (mass per unit length), the system of unit (SI) used is the tex (g/km). Textile strength is expressed as force per linear density (N/tex), and when mechanically quantified by specific stress, modulus and strength it is measured in tenacity [13]. Decitex, or dtex, is the most commonly used term to quantify fiber size and is measured as the mass in grammes per 10,000 meters. Common fiber sizes come in the range of 1-20 decitex (dtex), which corresponds to diameters of between 5 to 20 µm. Nanofibers have a linear density ranging from $10^{-3}$ to $10^{-7}$ dtex (3-300 nm).
Melting temperature, $T_m$ and glass transition temperature, $T_g$ are critical thermal properties for the characterisation of textile materials [12]. $T_m$ is a thermal property of a polymeric material that initialises a liquid state of that material. $T_g$ is the temperature where the chains in a thermoplastic material begin to loosen and vibrate, therefore permitting movement of the material, and an effect on textile elongation is therefore initialised. $T_g$ is only a characteristic of thermoplastic polymers and not of thermoset polymers. A detailed description of the properties of thermoplastic and thermoset polymers, including the thermal effects is provided in Section 2.1.6.

Mechanical properties are an important factor in any textile material, where fibre failure must be prevented. Strength, elasticity and abrasion resistance retain increasing importance as mechanical properties. The textile strength is examined by a combination of fibre material and processing, where the strength of any textile can be increased by twisting its yarns [1, 13]. Essential properties and the preferred measurement of popular textile materials are categorised in Table 2.1, where textiles of interest to the present study are highlighted.

<table>
<thead>
<tr>
<th>Polymeric Textile Material</th>
<th>Density (g/cm³)</th>
<th>Break Strength (MPa)</th>
<th>Elongation at Break (%)</th>
<th>Impact Strength (J/cm)</th>
<th>Melt Temp. (°C)</th>
<th>Glass Transition Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6/66</td>
<td>1.13 - 1.15</td>
<td>76 - 94</td>
<td>44 - 47</td>
<td>0.29 - 1.12</td>
<td>215/260</td>
<td>70</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>0.9 - 0.91</td>
<td>71</td>
<td>17</td>
<td>0.41 - 0.64</td>
<td>165</td>
<td>-10</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>1.2</td>
<td>50 - 72</td>
<td>80 - 140</td>
<td>6 - 8.5</td>
<td>260</td>
<td>150</td>
</tr>
<tr>
<td>Polyester (PE)</td>
<td>1.39</td>
<td>48 - 72</td>
<td>30 - 300</td>
<td>0.13 - 0.37</td>
<td>260</td>
<td>80</td>
</tr>
<tr>
<td>Polyvinylchloride (PVC)</td>
<td>1.2 - 1.5</td>
<td>30-60</td>
<td>20 - 40</td>
<td>1-3</td>
<td>100 - 260</td>
<td>80</td>
</tr>
<tr>
<td>Acetate</td>
<td>1.22 - 1.34</td>
<td>13 - 62</td>
<td>24</td>
<td>0.2 - 2.6</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Acrylic</td>
<td>1.19</td>
<td>69</td>
<td>25</td>
<td>2.16</td>
<td>170 - 190</td>
<td>115</td>
</tr>
<tr>
<td>Cotton</td>
<td>1.52</td>
<td>5.1</td>
<td>5.6</td>
<td>3.9</td>
<td>200 (chars)</td>
<td>-</td>
</tr>
<tr>
<td>Silk</td>
<td>1.34</td>
<td>60</td>
<td>23</td>
<td>7</td>
<td>175 (chars)</td>
<td>-</td>
</tr>
<tr>
<td>Wool</td>
<td>1.3</td>
<td>38</td>
<td>43</td>
<td>2.3</td>
<td>130 (decompose)</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.1 Thermal and mechanical properties of common polymeric textiles compared to natural fibrous textiles. Reproduced from reference [1, 11, 12, 14, 15]. Textiles of interest to the present study have been highlighted.
Properties including high impact strength yield a rigid and uncomfortable fabric. Nylon 6/6 and PE are popular materials employed in the textile industry, as they have good impact strength and elongation at the break. PE has a tensile strength of between 48 to 72 MPa, and very good elasticity of between 30 to 300% before fracture, as detailed in Table 2.1. Acetate and acrylic have similar properties to PE, which make them popular materials in the medical industry. More natural textiles like silk and wool have good elongation, while cotton had low elongation. The thermal properties of silk and wool are poor due to the organic nature of the structure.

The elastic behaviour of some common synthetic and natural textile fibers was presented in Figure 2.2. Textile fibres made from PE staple permit high elasticity during initial loading, while high-tenacity PE permit poor elasticity over high loads. Highly elastic fibres inherit crease resistance, bulkiness and dimensional stability properties [1], properties that are advantageous during the manufacturing and finishing processes of textiles.

![Figure 2.2 Stress versus elongation curves for synthetic fibers compared to common natural fibres. Reproduced from reference [1].](image-url)
2.1.2. Medical Textiles

Textile technology dates back over 10,000 years. Since antiquity, textile design has been dominated by natural fibres such as cotton wool and silk. In recent times, synthetic fibres have been introduced. Table 2.2 described new processes, materials and applications that were considered as milestones in the development of technical textiles [11]:

<table>
<thead>
<tr>
<th>Period</th>
<th>Yarn Type</th>
<th>Purpose</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antiquity</td>
<td>Cotton, flax</td>
<td>Rope, twine</td>
<td>Heavy weight, microbial attack, hydrophilic</td>
</tr>
<tr>
<td></td>
<td>Jute</td>
<td>Furniture, sacking,</td>
<td>Coarse, strong threads. Cheap. Sound and heat insulation. UV protection</td>
</tr>
<tr>
<td></td>
<td></td>
<td>carpets, felt</td>
<td></td>
</tr>
<tr>
<td>Viscose rayon</td>
<td>Rubber belts, hoses, conveyors, tire cord</td>
<td>Cool, comfortable, hydrophobic, poor durability</td>
<td></td>
</tr>
<tr>
<td>Polyamide (nylon)</td>
<td>Rope, parachutes, ladies apparel</td>
<td>High strength, elasticity, hydrophobic, abrasive.</td>
<td></td>
</tr>
<tr>
<td>Polyester (PE)</td>
<td>Household furniture, reinforcement, containers</td>
<td>Strength, abrasion, wrinkle resistant, hydrophobic, uncomfortable to skin</td>
<td></td>
</tr>
<tr>
<td>Polyolefin</td>
<td>Bags, carpet underlining, rope, netting</td>
<td>Low density, good abrasion, easy manufacture, hydrophobic, cheap</td>
<td></td>
</tr>
<tr>
<td>Kevlar, High performance PET, glass fiber</td>
<td>Bullet proof vests, rope, protective clothing, reinforced tyres</td>
<td>Heat-resistant, high strength, hydrophilic</td>
<td></td>
</tr>
<tr>
<td>Ultra strong and high modulus PET, polytetrafluoroethylene -lene (PTFE)</td>
<td>Rope, ballistic protection, non-stick coating in cookware, unreactive</td>
<td>Flameproof, heat resistant, hydrophobic, chemical containers and pipework</td>
<td></td>
</tr>
</tbody>
</table>

High performance fibres were designed for properties of extraordinary strength, stiffness, abrasion, chemical and heat resistance. Poly-paraphenylene terephthalamide (PPDT), trademarked Kevlar™ was the most notable breakthrough of these high performance fibres [1]. PET, polypropylene (PP), polyamide, carbon and fibreglass were just some of the increasingly popular synthetic fibrous materials.
in use as devices. A combination of performance, aesthetics and functional properties of textiles initiated a radical change of industrial and public perception of textile materials.

Textile materials employed in the medical, applied healthcare and hygiene sectors are currently an important and growing part of the T&C industry. Categories of medical textiles include; non-implantable, implantable, extracorporeal devices, healthcare and hygienic products [11, 18]. This is an area that all countries have promising growth prospects due to longer-life, increasing affluence and interest in health [19]. The sector offers scope in terms of research and innovation for technical textile applications.

Hygiene applications, which are dominated by non-woven textiles such as wipes, baby nappies and adult sanitary products account for the largest use of textiles and the greatest amount of non-disposable waste [11]. The classification of commercially known medical textiles includes, but is not limited to the list in Table 2.3:

<table>
<thead>
<tr>
<th>Definition</th>
<th>Yarn</th>
<th>Purpose</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbents</td>
<td>Cotton</td>
<td>Absorb moisture, eliminating bacteria</td>
<td>Hydrophilic, sterile</td>
</tr>
<tr>
<td>Dressing retention and wound dressing</td>
<td>Acrylic, cotton, PET, poly/cotton</td>
<td>Bandages, tapes for holding dressings, catheters and pipes</td>
<td>High strength, long lasting adhesion</td>
</tr>
<tr>
<td>Padding</td>
<td>Cotton, poly/cotton</td>
<td>Orthopedic bandages, fiber pads, adhesive tape</td>
<td>Friction and pressure relief</td>
</tr>
<tr>
<td>Support Bandages</td>
<td>Cotton, poly/cotton</td>
<td>Calico or prep bandages to hold splints</td>
<td>Strength</td>
</tr>
<tr>
<td>Drapes, gowns, surgical apparel</td>
<td>Cotton, PET, poly/cotton, polypropylene</td>
<td>Barrier resistance to liquids, microbes</td>
<td>Hydrophobic, sterile, high strength, comfort</td>
</tr>
</tbody>
</table>

Table 2.3 Classification of commercially known medical textiles. Reproduced from references [11, 18]
Health and hygiene textiles incorporate garments that may constitute protection of a user from the potential dangers that are present in a medical environment [18]. As a result of bacterial contamination in hospitals, barrier efficacy of textiles is paramount [20]. Surgical gowns and drapes made from textiles are employed in medical environments for the prevention of bacterial contamination [21]. They are manufactured from either non-woven or woven textiles. Non-woven textiles are designed for single-use and are usually designed for disposable use [22], while woven gowns can be reused after laundering and sterilisation [23]. Reusable textiles pose a performance risk, as single-use textiles were reported to maintain manufacturer's specifications better than reusable textile products [24, 25]. Here, the growth of disposable products within the textile industry was an increasing ecological concern [26]. Large development has been undertaken to permit development of biodegradable and reliable reusable fibres [27].

2.1.3. Microbial Interactions with Textiles
Biofouling formation is the accumulation and limitation of the adhesion of microorganisms on wet surfaces [28]. The prevention or limit of microbial initialisation to surfaces has a major impact on medical devices, food processing equipment, heat exchangers, cooling water systems and ship hulls. Through chemical interactions and forces, the molecules or atoms on a surface usually interact with the molecules or atoms in a solution. Dust, liquids and fluids such as blood and perspiration are seen as methods of transport for bacteria through textiles [29]. The financial, societal and personal cost of microbial infections to patients and hospitals was difficult to compare between studies, as these studies are achieved over different periods of time in countries with varying qualities of healthcare systems.
2.1.4. Microbial Characteristics and Surface Contamination of Textiles

Microbes can be defined by three categories; bacteria, fungi and algae. Bacteria and fungi only apply to textiles [28, 30]. The differences between bacteria and fungi are outlined in Table 2.4 below:

<table>
<thead>
<tr>
<th>Microbe</th>
<th>Description</th>
<th>Causes</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacteria</td>
<td>Simple structure/fast growing in warm and wet conditions</td>
<td>Unpleasant odors (e.g. E. coli)</td>
<td>Antibacterial Agent</td>
</tr>
<tr>
<td>Fungal</td>
<td>Complex structure/slow growing</td>
<td>Staining and loss of performance. Skin infections (e.g. athletes foot and Candida)</td>
<td>Antifungal agent</td>
</tr>
</tbody>
</table>

Textiles treated with antimicrobial agents assist in both the prevention and control of cross infection by preventing microbial growth. Antimicrobial materials employed in the preparation of textiles can be classified into “static” and “cidal” categories [3, 31], with the main differences presented in Table 2.5. More traditional treatments tend to be in the “cidal” category, and due to the leaching action, they need to be evaluated for the effects on health and safety. Recent research is leaning towards “static” type agents as they are deemed to be of reduced risk.

<table>
<thead>
<tr>
<th>Antifungal and Antibacterial Agents</th>
<th>‘Static’ Agents</th>
<th>‘Cidal’ Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-leaching or “bio-static” – results in a textile surface that inhibits microbial reproduction</td>
<td>Leaching – diffuses out of the fabric and kills any microbes, inhibiting further growth</td>
<td></td>
</tr>
<tr>
<td>Slower acting: work by inhibition of microbial growth</td>
<td>Increased reaction: causes severe destruction of microbes</td>
<td></td>
</tr>
<tr>
<td>Good Durability: reduced H&amp;S risk. Increased microbial development to resistance</td>
<td>Reduced durability: Potential high H&amp;S risk. Decreased microbial development of resistance</td>
<td></td>
</tr>
<tr>
<td>Example: silver based compounds, Tributylin maleate – controls bacterial and fungal growth</td>
<td>Example: Chloroxynol (both fungicidal and bactericidal)</td>
<td></td>
</tr>
</tbody>
</table>
The effect of surface roughness on the adhesive attraction of bacteria to a polymer material has been well documented [34, 35], with less knowledge available to the effect that chemical properties of polymers permitted on bacterial adhesion. Focusing on chemical properties, clinical grade polymers and polymeric films deposited by spin coating (PMMA, LDPE and PVC) were studied for the initial events and process responsible for bacterial adhesion. The chemical interaction during the initial contact between the bacteria and the polymer surface was a defining factor, with increasing risk of colonisation and bio-film formation. With various surface energies, *E. coli* adheres to polymeric coatings that were in contact with a stainless steel substrate. This indicates that bacterial adhesion is related to the increase of a substrates interaction energy. A 95% reduction of *E. coli* was recorded on antibacterial polymer coatings [36], where the coating primarily consisted of polyethylene tetrafluoroethylene (PTFE).

 Personnel protection equipment (PPE), such as surgical gowns and drapes worn by hospital staff in a health care environment have been considered a major transporter of hospital acquired infections (HAI). The use of hands has been considered a major instigator in the habitation of microbes to PPE, with studies proving bacterial contamination of PPE by the use of hands [29]. The most notable PPE that transports HCAIs’ were gowns and drapes worn by hospital staff, as these materials frequently contacted the hands of health care workers [37]. Gowns worn by hospital personnel in an intensive care unit (ICU) were analysed at stages of a working period, where long sleeved gowns were examined at the cuffs and short sleeved around the abdominal area, i.e. these been the areas in contact with the wearer’s hands. Studies have recorded large populations of microorganisms on hospital gowns before working periods, where these populations greatly increased by the end of that working period [38, 39]. Bacterial counts reported in the abdominal region of the gowns were greater than that recorded at the cuff area.
2.1.5. Classification of Synthetic Fibers

The structure and characteristics of synthetic textiles popular to medical environments are discussed. The textile fiber industry has been dominated but not limited to a small number of chemical types, as listed in Table 2.6.

Table 2.6 Chemical types of common fibers in the textile industry. Reproduced from reference \[1, 13, 40, 41\]

<table>
<thead>
<tr>
<th>Chemical Type</th>
<th>Fiber</th>
<th>Structural Formula of Fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate (PET)</td>
<td>![Structural Formula of PET Fiber]</td>
</tr>
<tr>
<td>Polyolefin</td>
<td>PP</td>
<td>![Structural Formula of PP Fiber]</td>
</tr>
<tr>
<td>Polyamides</td>
<td>Nylon 6</td>
<td>![Structural Formula of Nylon 6 Fiber]</td>
</tr>
<tr>
<td></td>
<td>Nylon 6,6</td>
<td>![Structural Formula of Nylon 6,6 Fiber]</td>
</tr>
<tr>
<td>Cellulose</td>
<td>Cotton, rayon, cellulose acetate (CA)</td>
<td>![Structural Formula of Cellulose Fiber]</td>
</tr>
</tbody>
</table>

A traditional material, such as PE is employed to produce textile yarns. PE falls in the scope of thermoplastic polymers, which is defined as a series of long flexible chains made up of identical repeat units of linear monomers, held together by secondary bonds in the form of Van der Waals bonding. Linear polyethylene terephthalate (PET) is the most widely used PE fiber.
The easy alignment of linear chains in PET makes it an almost fully crystalline structure, as presented in Table 2.6 [1]. The linear chains readily permit crystallisation, even when fast cooling of the structure initiates. The long chains instil highly elastic properties into fibers. PET fibers have properties including strength and hydrophobicity, which are beneficial when durability during wet and dry conditions is required. PET characteristics of benefit to medical environments are listed as [1, 13];

- Strength of fibers in wet and dry conditions
- Easily cleaned
- Bacterial resistant
- Wrinkle resistant
- Good abrasion
- Fast drying
- Resistance to most decomposing chemicals

Polyolefin fibers are short repeat units without interactive groups, as presented in Table 2.6. They consist of long chains of a synthetic polymer with at least 85 wt.% ethylene, propylene or other olefin units [40]. PP is currently the most popular of polyolefin fibers due to its crystallinity, when compared to other rubbery polymers derived from propylene. Tenacity, abrasion resistance, elasticity and strength of PP fibers are similar when compared with PE fibers, while PP has reduced density and melting temperature [40]. The cheap cost of PP fibers is unstable, as it is solely dependent on the refinery cost of propylene and the various additives required for manufacturing. Characteristics of PP are [12];

- Low melting temperature
- Poor moisture absorption
- Poor dyeing properties
- High property failure at low temperatures
- Uncomfortable texture of fiber

Nylon is a popular polyamide fiber, which was the first to be manufactured from petroleum products. They are a combination of monomer units joined by amide groups [40]. The chemical formula of nylon 66 and two repeats of nylon 6 are
presented in Table 2.6. Nylon 6 & 66 both have the same number of units, with a difference in the absence of symmetry present in nylon 66. Crystal packing of the nylon 66 can be affected, and thus nylon 6 has a reduced melting temperature. The elastic modulus of nylon is highly dependent on temperature, where large shrinkage of the fibers permits initiation at moderate temperatures, while straining the fibers increases the length and modulus of the fiber [13]. Characteristics of nylon fibers are listed [13, 40];

- Tough and durable
- Good comfort due to high elasticity
- Abrasion resistant
- Poor wetness properties, affecting the critical temperatures and strength

Cellulose is derived from plants, where it is the main structural material. It is a condensation polymer formed by biosynthesis from carbon dioxide and water, where glucose is the intermediate monomer [40]. The molecule is ribbon-like, which permits easy twisting and bending in a single plane. Biosynthesis initiates at enzyme complexes within plant cells. Natural cellulose fibers can be regarded as fully crystalline, where glucose units add on to thirty growing molecules which automatically crystallize as fibrils at each complex [13]. Viscose rayon (VR) and CA are popular chemical fibers based on natural polymers. Rayon is employed in various nonwoven fabrics for its strength and crease resistance when wet. CA is an aesthetically pleasing textile, where it is employed in upholstery and drapery. Its characteristics include [12];

- Good comfort and strength
- Whiteness
- Poor resistance to abrasion

Cotton is a natural fiber of vegetable origin, and is deemed the most important of its type, where it is grown from 95% cellulose extracted from the cotton plant [40, 42]. The 5% retained consists of noncellulosic materials, mostly located at the primary wall of the fiber, consisting of proteins, natural waxes and peptic substances. Cotton cellulose is a naturally occurring polymer, where the molecular chains are of varying lengths, as presented in Table 2.6 [13]. Cotton fibers are popular for their comfort and aesthetic qualities. The inherent hydrophilic properties
lead to a reduction in modulus as mobility of fibrils is increased [42]. Elongation at the break is reduced with an increase in the humidity. Unusually, as with most natural plant fibers, increasing fiber wetness leads to an increase in strength of the fiber. The main characteristics of cotton fibers are listed [13, 42];

- Absorbent
- Good strength
- Comfortable and aesthetically pleasing
- Retention of colour

Blending of two or more textile yarns is a popular technique that utilises advantageous properties from each of the textile blends [2]. Cotton is a popular yarn used to blend with synthetic textiles such as PET, forming the combination known as poly/cotton. For example, PET can assist with retention of fabric shape and resistance to wrinkling [1], while the cotton yarns permit a contribution of absorbance and comfort to the composite fabric [42].

2.1.6. Thermal Properties of Polymeric Textile Materials

The thermal properties of a polymeric textile are essential to the textiles end-use functions. The mechanical performance of a textile is changed as its critical temperatures are exceeded [43]. $T_m$ is a critical temperature of a polymeric material, where this temperature is the highest limit of the materials performance and integrity. $T_m$ depends on details of the polymers carbon chains and formation of these chains [12]. The chain form can be linear, branched or cross-linked, and a great variety of chemical groups can be linked to the chain backbone. If chains are sufficiently aligned, they permit the formation of repeating units, or they enable intertwining of amorphous regions. A fully crystalline structure known as a thermoset is composed of linear chains, and is therefore denser than an amorphous structure of the same material. Thermosets are non-reversible, as they become hard when heated and do not permit softening upon reheating [1, 12]. An increase in the molecular weight generally permits an increase in the impact strength of a polymeric material [43]. Chemical structure, molecular mass and degree of branching also control the melting point of a polymer, where multiple chain-ends from low molecular mass initiate a result in a low $T_m$. 

23
Thermoplastic textiles are a soft and ductile material, with PET, polystyrene (PS), CA, nylon, acrylic, and PP been common examples. Thermoplastic materials are a mixture of crystalline and amorphous regions consisting of linear chains, with side branches that can also cross-link monomers, as presented in Figure 2.3 [1]. Polymers that contain amorphous regions permit a gradual softening to a rubbery state, which is characterised by the glass transition temperature, $T_g$ [1, 44]. The process termed, viscoelastic behaviour, is totally reversible and repeatable up to but not exceeding the $T_m$ of the polymer.

Viscoelasticity is a property of a polymer that inherits both viscous-like and elastic properties under load [9]. At low temperature, secondary or non-covalent bonds form between adjacent chains in a thermoplastic material. When the temperature rises to $T_g$, the increasing molecular motion eventually breaks secondary bonding between chains, thereby creating disorder in the structure. Activation of the chains are enabled, allowing them to slide past each other when a force is applied, and initiating flexibility and elasticity of the fibres above this temperature. The polymer permits elastic properties upon loading, where a slow and continuously increasing strain-rate is initiated. Upon unloading of the polymer, an initial elastic recovery is present, and a continuously decreasing strain is initiated. At $T_m$, the polymer chains go from an ordered to highly disordered state, where the process becomes irreversible due to the breakdown of covalent bonds.

![Figure 2.3 Schematic structure of a thermoplastic polymer, illustrating amorphous and crystalline regions [45].](image)
$T_g$ is highly dependent on chain flexibility and the ease of rotation about the chains chemical bonding [43]. Increasing crystallinity permits stiffening of the amorphous phase, and a reduction of flow of chains. Polymers with chemical formulas containing –O-, -O-O-, -CO-O have increasing flexibility [12]. As side groups reduce chain flexibility, PP is therefore less flexible than PET. $T_g$ can be considered as important as $T_m$ in many functions of technical textile fibers. Physical properties such as stiffness, will steadily change before the $T_m$ of a thermoplastic is reached [9].

A slight change in temperature initiates a rapid decrease of the elastic modulus in an amorphous polymer, when it changes from a glassy to a rubbery state [9]. Exceeding the $T_g$ of an amorphous polymer permits an increasing effect on its viscoelastic behaviour [9, 12]. The effect of temperature to specific volume for amorphous, semi-crystalline, and crystalline polymers is presented in Figure 2.4 [1, 9, 43]. The specific volume of a polymer is important when considering the shrink rate of a textile fabric. More distinct steps can be identified as:

a) An amorphous structure is hard and glossy at temperatures below $T_g$, while between $T_g$ and $T_m$ the polymer becomes rubbery.

b) A semi-crystalline polymer is a glassy solid below $T_g$, a rubbery solid that increases in specific volume between $T_g$ and $T_m$, where it changes from a solid to liquid state above $T_m$.

c) A crystalline polymer acts as a crystalline solid below $T_m$. It has no $T_g$ and is in a liquid state above $T_m$, where the specific volume increases.

![Figure 2.4 Specific volume versus temperature, upon cooling from the liquid melt, an amorphous (a), semi-crystalline (b), and crystalline polymers (c). Adapted from [1].](image-url)
The dependence of temperature, $T$ on the response of a polymer is highlighted by the large effects presented on their mechanical properties [46]. An understanding of the viscoelastic behaviour is integral to the effective and efficient use of the functions. A profile displaying viscoelastic behaviour of the tensile relaxation for both amorphous and semi-crystalline polymers at levels of temperature, $T$ and time, $t$ were presented in Figure 2.5.

![Figure 2.5 Schematic of elastic modulus versus temperature curve, presenting regions of viscoelastic behaviour. Adapted from [9]](image)

At low temperatures, the polymer in the glassy region, termed $E_1$, above $10^9$ Pa, is hard and brittle. Polymer chains in this section are practically frozen in position, as the thermal energy is insufficient to overcome the rotational and translational barriers [9]. Upon reaching $T_g$, the amplitude of vibrational motion increases, where the chains increasingly vibrate and the brittle glass becomes a tough viscous rubber like material. At this point the modulus decreases rapidly, where it then stagnates until just before $T_m$ is reached, which is termed as modulus $E_2$. The polymer is not yet fully viscous as there still exits strong local interactions between neighbouring chains, which take the form of primary bonds in semi-crystallised materials [1, 44].
The viscoelastic behaviour of crystallised and semi-crystallised structures in the rubbery section is almost identical. As temperature increases, the primary bonds remain intact where a minimal reduction in modulus is permitted until chemical degradation initiates at $T_m$. The linear chains of thermoset polymers permit increasing molecular motion with an increase of temperature, until they eventually translate and are no longer capable of preventing molecular flow [9]. At this point the thermoset polymer is experiencing molecular flow and does not permit recovery, but relaxes to a new state with increasing length upon cooling. If the polymer material surpasses $T_m$, the disordered state and sliding chains then take full effect [1, 9]. At this point the polymer becomes liquid if it has not initiated chemical reaction, and the polymer no longer has any strength.

2.1.7. Barrier Properties of Textile Materials

The inherent properties of textile fibers have provided an environment for the growth of bacteria. Humidity and warmth have further aggravated this problem, where staining and the loss of performance of the dependent properties of textiles have been initiated due to microbial attack [47]. The antimicrobial ability of woven gowns has been studied for staphylococcus aureus (SA). Gowns were analysed at 0, 25 and 50 commercial cycles of laundering [24, 48, 49]. Surgical gowns presented no significant change of weight and thickness after 50 cycles of laundering. 50/50 poly/cotton gowns permitted significant reductions in oil and water repellancy, while porosity of PET gowns increased after laundering. The increasing porosity of the gowns was attributed to the added flexibility of the fabric structure after laundering. Gowns also retained an increasing rate of repellancy and fibre thickness, which was a contribution of the increasing barrier properties. PET and poly/cotton blends of gowns allowed penetration of bacteria before cycles of laundering. Bacterial penetration of the gowns increased as a result of the reduced functional properties due to laundering. 99/1 poly/cotton gowns permitted no increase of bacteria content after laundering.

Woven gowns have been known to have poor barrier properties, even before they undertake cycles of laundering [50]. Gowns with a coating permitted retention of liquid and microbial barrier properties after 80 cycles of laundering. Fabric
construction, water repellancy and pore size were found to be critical characteristics of barrier properties of surgical gowns. Woven gowns presented increased water repellancy and reduced oil content over nonwoven gowns [25], which was a factor of the woven fabrics reduced pore size and hydrophobic nature. When a bacterium was carried by water, the difficulty of flow through the textiles was increased with the reduced sizes of pores. Therefore, a less porous woven gown will reduce the flow of water.

2.2. Nanoparticles with Antimicrobial Properties

Materials exhibiting advanced chemical and physical properties while in the nanoscale are known as NPs or also known as engineered nanomaterial’s (ENMs). Nanotechnology is the deliberate synthesis and control of such NPs. Nanotechnology was first termed in 1974 by Professor Norio Taniguchi [51], in an article called “The Basic Concept of Nanotechnology.” Eric Drexler, an American Engineer published the 1st paper on Molecular Nanotechnology, and in 1986 wrote the first book on Nanotechnology [52], titled “Engines of Creation: The Coming Era of Nanotechnology.”

Many materials are inert at the macroscale size, but when the size reaches the nanoscale they can display extraordinary properties due to the size [53]. NPs are manufactured in a range of differing elements [54], shapes, and sizes for use in a wide range of products and industrial processes that utilise the novel physical, thermal, optical, and biological properties [33]. Such properties can be examined by the chemical composition of NPs, size or shape, crystal structure, solubility, adhesion, surface chemistry, charge or area. As the size of NPs reduces the surface area to volume ratio (SA/V) increases, and permits a larger surface area for a given volume. NPs often permit reactions with increasing speed and provide increasing chemical reactivity due to the larger surface area providing an increase in the reaction sites for the same volume [32]. Nanotechnology greatly increases a material or chemical’s SA/V.
The fast emergence of nanotechnology indicates the beginning of a technological revolution that will greatly benefit aspects of everyday life [55]. The aggressive growth of the two leading technologies, biotechnology and information communications technology (ICT) require nanotechnology to sustain and lead a techno-economic transition. Nanotechnology can be categorised in the following domains [55, 56]:

- Bionanotechnology; molecular scale properties and applications of biological nanostructures.
- Nanoelectronics; properties and applications of semi-conductor structures and devices.
- Nanomaterials; control of the structure of materials at the nanoscale.
- Nanomanufacturing and tools; more intricate nanostructures and characterising.
- Nanotextiles; the incorporation of nanomaterials into or on the surface of a textile fiber, or production of a fiber in the nanoscale.

### 2.2.1. Antimicrobial Abilities of Nanoparticles

NPs that display photocatalytic properties require a particular band-gap of light for activation, which in optical terms is the wavelength (\(\lambda\)) of light. These NPs are known as a semiconductors and act as the catalyst, while photons of light provide the required band-gap energy (\(E_g\)) [57]. The reaction that displays light absorption of a semiconductor catalyst is presented in Figure 2.6.

![Figure 2.6 Schematic displaying light absorption from a semiconductor catalyst. Adapted from [45].](image-url)
Absorption of photons will initiate in the presence of UV light [58, 59], with differing elements having specific $E_g$ and absorption at specific wavelengths. A semiconductor is nonconductive until its $E_g$ is reached. An electron is then excited and transported from the valence band to the conduction band. This is achieved by absorption of a photon of energy equal to or greater than the $E_g$ of the semiconductor. The relationship between energy transition and wavelength can be expressed as Eq. 2-1 [3, 45]:

$$E_g = h\nu = \frac{h}{\lambda}$$  \hspace{1cm} (2-1)

Where, $h$ is Plank’s constant, $\nu$ the velocity of light, and $\lambda$ is the specific wavelength. Organic compounds are sensitive to contact with such a reactive surface [3]. The presence of a strong oxidation effect through photocatalysis, contributes to photoelectrochemical reactions that can decompose soilage, harmful bacteria and organic contaminants into carbon dioxide and water [58, 59].

NPs are widely known to exhibit antimicrobial properties. Nanoscale TiO$_2$ [3, 32], carbon nanotubes (CNT’s) [60, 61], ZnO [62, 63], gold Au [53] and silver (Ag) [64-66] are just some of the more common NPs that exhibit such properties. The antimicrobial action of TiO$_2$ and ZnO stems from photocatalytic properties [3, 67], while CNT’s inherit antimicrobial activity from the shape, morphology and chemical structure of the NPs [68]. Gold, Cu [53, 69, 70] and Ag [64, 65], can be activated through metal ion release. Popular NPs and method of activation were listed in Table 2.7.

<table>
<thead>
<tr>
<th>ENM</th>
<th>Method of Antimicrobial Activation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Photocatalysis in the UV spectra</td>
</tr>
<tr>
<td>Silver</td>
<td>Metal ion release, shape, photocatalysis</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Shape, morphology and chemistry</td>
</tr>
<tr>
<td>ZnO</td>
<td>Photocatalysis. Structurally dependent</td>
</tr>
<tr>
<td>Gold</td>
<td>Metal ion release, shape size and morphology</td>
</tr>
<tr>
<td>CuO</td>
<td>Metal ion release, shape size and morphology</td>
</tr>
</tbody>
</table>
2.2.2. *Titanium Dioxide (TiO₂) and Photocatalysis*

TiO₂ has two distinct photoinduced phenomena; firstly its ability to break down organics; and secondly its super-hydrophilicity [57]. These two processes may have varying levels of each property, but they must take place at the same time. Ti illuminated by sunlight presents a change in colour from white to grey, blue or black, indicating a partial reduction of Ti. When oxides such as TiO₂ and ZnO, known as a semiconductor catalyst (SC) are illuminated with photons whose energy is equal to or greater than the band-gap energy \((hν \geq E_G)\), absorption of photons takes place on the particle surface [3, 32, 33, 57].

TiO₂ is a SC with a band-gap energy of 3.2 eV or greater, and its reaction process is presented in Figure 2.7. Photonic activation of the SC permits generation of an electron hole pair on surfaces of TiO₂-NPs when they are excited by light with a wavelength of 385 nm. The hole in the valence band reacts with H₂O or hydroxide ions absorbed on the surface to produce hydroxyl radicals (OH⁻), and the electron in the conduction band can reduce O₂ to produce superoxide ions \((O₂⁻)\) [58, 59].

![Figure 2.7 Schematic illustration of the photocatalysis process of TiO₂-NPs. When illuminated with light of energy greater than the band-gap, electron and holes are formed in a semiconductor and are capable of initiating chemical reactions [71].](image)

TiO₂ is considered to be the most economically viable photocatalytic material, and described as having the most efficient photoactivity and the highest
stability. UV light irradiation of TiO$_2$ came to attention through the discovery of paint degradation in sunlight [72], while holding its chemical stability in darkness. Powders of TiO$_2$ were dispersed into alcohol and hydrocarbon solvents, and subjected to UV light irradiation. The outcome was an auto-oxidation of the solvents and the formation of H$_2$O$_2$ [58]. One of the first commercial applications to use nanotechnology involved the use of TiO$_2$ surfaces as a self-cleaning technique on the cover glass fitted to highway tunnel lamps [73-75]. UV light emitting 3 mW/cm$^2$ was sufficient to decompose contamination from exhaust fumes on the cover glass. TiO$_2$ can only use a small quantity of solar light energy density, owing to inadequate activity for the acquisition of energy or the treatment of large volumes of water and air.

The superhydrophilic property of TiO$_2$ is the property of having high wettability, or a contact angle approaching zero. The presence of UV light is required for this action to permit an even spread of water across a surface [57]. The discovery of photoinduced superhydrophilicity has broadened the application range of composite materials of TiO$_2$ [72]. This property can be utilised to displace organic compounds on its surface. The photonic excitation of NPs, with the aid of rainwater has led to the utilisation of TiO$_2$ photoinduced superhydrophilicity in outdoor applications such as glass, mirrors, exterior tiles and PVC fabric. The superhydrophilic reaction of PVC and glass is presented in Figure 2.8. Water flow is employed as a productive catalyst for TiO$_2$ to release soilage from a surface [2, 74, 76]. This reaction is a result of water penetration at the molecular level space, in-between the soilage present on the surface and the superhydrophilic surface of TiO$_2$.

![Figure 2.8](image.png)

Figure 2.8 Conventional PVC tent material (left), and TiO$_2$-coated tent material (right) (a). Anti-fogging effect of automobile side-view mirror: conventional mirror (left) and TiO$_2$ coated mirror (right) (b) [72].
Superhydrophilic and organically decomposing NPs are now incorporated in numerous consumer products to instil self-cleaning properties. The most popular of those products and the NPs that has best suited that area were presented in Table 2.8.

Table 2.8 Products available to consumers with self-cleaning properties. Reproduced from [54, 77].

<table>
<thead>
<tr>
<th>Category</th>
<th>Area</th>
<th>ENM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roads and Houses</td>
<td>Lighting, walls, roofing, windows, traffic signs</td>
<td>TiO₂, Silver</td>
</tr>
<tr>
<td>Electrical equipment</td>
<td>Computer display, cover glass for solar cells</td>
<td>MWCNT, Silver</td>
</tr>
<tr>
<td>Vehicles</td>
<td>Paint work, windows, headlights</td>
<td>Silver, TiO₂</td>
</tr>
<tr>
<td>Consumer products</td>
<td>Table and kitchen ware, antifouling spray-on coatings</td>
<td>Gold, ZnO, Silver, TiO₂</td>
</tr>
<tr>
<td>Medical Equipment</td>
<td>Gowns, drapes, bandages, wipes</td>
<td>Copper oxide, Silver, TiO₂</td>
</tr>
</tbody>
</table>

Three main types of TiO₂ structures exist; anatase, brookite and rutile. Rutile NPs greater than 35 nm in size is the most stable phase. Anatase has increased stability at sizes less than 11 nm, and in the 11 to 35 nm range brookite was considered to permit increasing stability [48, 78]. The chemical structures of anatase, brookite and rutile are presented in Figure 2.9.

![Chemical structure of anatase (a), brookite (b) and rutile (c). Reproduced from [32, 57, 79].](image-url)
The exposed atoms of Ti are low on electron density. Anatase has two low energy faces, where (101) is the most common nanocrystal [32, 80], Figure 2.9(a). It contains alternating rows of 5-coordinated atoms of Ti and bridging oxygen situated at the edge of corrugations. Brookite is an increasingly rare type of nanocrystal due in part to its difficulty of preparation [32], Figure 2.9(b). Synthesis of Brookite requires high temperature and processing of pressure [3, 32]. Rutile contains three main crystal faces, where (110) is the most thermally stable. It contains two atoms of Ti connected to rows of bridging oxygen’s, where the corresponding atoms of Ti are 6-coordinate, Figure 2.9(c). There are rows of 5-coordinate atoms of Ti running parallel to the rows of bridging oxygen’s and alternating with these.

A number of active oxidative species are involved in the initiation of photocatalytic oxidation reactions, offering TiO₂ the ability to oxidise organic and polymeric materials, kill microbes and mineralise these substances with the aid of molecular oxygen. Reactions initiate on or close to the surface of the TiO₂-NPs. With wavelengths of less than 385 nm, TiO₂ has a high activity rate and good oxidising power, making it a strong photocatalytic material when illuminated by UV light [76, 81-83]. Photocatalytic ability of TiO₂ is dependent upon the energy of the incident photons, not on the intensity, resulting in photocatalysis been induced with just a few photons of the required energy. A small quantity of pollutant in air or on a wall may be decomposed with a sufficient quantity of conventional indoor room light [57].

Ti (DegussaTM) has permitted the most efficient photocatalytic performance with a maximum quantity of outputs of all the NPs that are available to the marketplace. Initial rates of a reaction are proportional to the mass of Ti, as presented in Figure 2.10(a). Above a certain value of mass of Ti, the reaction rates reach a finite level, and resist any increasing reaction to the mass. Geometry and working conditions of the photoreactor determine this limit. Values equal to 2.5 and 1.3 mg of TiO₂/cm² were correlated for a suspension and a fixed bed respectively [71]. Reaction rate as a function of wavelength follows the absorption spectrum of the Ti with a threshold corresponding to the Ti band-gap energy of 3.02 eV, and wavelength 385 nm, as presented in Figure 2.10(b) [71].
The low light energy density of TiO$_2$ in water and/or air has rendered it inefficient for thorough photocatalysis of a medium. This is a factor of the large three dimensional volume required for sufficient distribution of the TiO$_2$ that would allow for efficient photocatalytic activity to decompose an inorganic compound. A reduction of the surface area that targets substances absorbed on two-dimensional surfaces was deemed efficient for decomposition. Applying TiO$_2$-NPs to a substrate permits a reduction of the surface area that requires activation, therefore utilising the UV light intensity that exists in an ordinary environment [72]. TiO$_2$ has minimal ability to decompose a large existent volume of pollutant. If a surface coated with a catalyst is clean before contamination by a pollutant, TiO$_2$ is then capable of decomposing as it begins to accumulate. The oxidation power of TiO$_2$ on decomposed pollutants in the presence of an aqueous suspension of TiO$_2$ permit high reaction efficiency [84]. The outcomes indicate that hydrogen production technology is not suitable, due to the low proportion of UV light in the solar spectrum, approximately 4.5%.

2.2.3. *Antimicrobial Properties of Nanoparticles of TiO$_2$*

It is widely known that *E. coli* cells exposed to UV irradiation can completely decompose on surfaces of TiO$_2$ [58, 83, 85-87]. *E. coli* cell deactivation can take longer indoors, as UV light irradiation from popular halogen lamps is predicted to be lower than 1 µW/cm$^2$. 

![Figure 2.10 Influence of the different physical parameters which govern the reaction rate r (r is generally between 1 and 0.1 mmol/h): (a) mass of catalyst; (b) wavelength [71].](image)
Figure 2.11 Schematic illustrations of photokilling process for *E. coli* cells on TiO$_2$ irradiated film, light absorption of TiO$_2$ (a), outer membrane breach (b), and cytoplasmic membrane decomposition (c). Adapted from [32, 88].

a) Light energy of sufficient intensity and wavelength is illuminated on the NPs surface of TiO$_2$ and absorbed.

b) Photocatalysis by TiO$_2$ begins an attack on the outer membrane of the cell, and breaches it through peroxidation of the cell wall. Partial decomposition of the outer membrane changes the permeability of the reactive species. Here it produces hydroxyl radicals (OH$^-$), and superoxide ions (O$_2^-$).

c) The hydroxyl radicals then easily penetrate the cytoplasmic membrane, leading to peroxidation of the membrane lipid. The remainder of the cell then decomposes into CO$_2$ and H$_2$O.

Photocatalytic reactions by TiO$_2$ have a significant role in assisting the intrusion of copper ions into an *E. coli* cell, and enabling the killing of cells under weak UV light [87-89]. Copper (Cu)/TiO$_2$ deposited films decomposed *E. coli* cells under the presence of a weak UV light source after 2 hours of irradiation. TiO$_2$ dispersed in a media has extraordinary light scattering ability. As a finely divided powder, the whiteness of Ti comes from its high reflectance, and displays uniformity throughout the visible spectrum. Photocatalytic performance of TiO$_2$ depends on the
preparation method of the NP, the ratio between anatase and rutile crystal phases, temperature, particle and crystal size, annealing, surface area, light intensity and substrate to be degraded. Antibacterial effects of a range of sol-gel solutions of TiO$_2$ were analysed against the deactivation of *E. coli* cells. TiO$_2$ sourced from Degussa$^{TM}$ permitted the largest effect on the microbe. Photocatalytic activity of solutions of TiO$_2$ increased with an increasing concentration of NPs used, but was inversely proportional to the particle size [90]. As a result of the wide band-gap, both anatase and rutile structures of TiO$_2$ mostly absorb UV photons. With solar light containing only 4.5% of UV photons, and standard artificial light emitting visible photons [23, 91, 92], increasing the spectral response of pure TiO$_2$ towards visible light is an active area of research. Doping of TiO$_2$ with metal impurities, non-metal atoms, coupling with narrow band gap semiconductors, and preparing oxygen deficient TiO$_2$ were methods explored in the area of widening the spectral response.

2.2.4. Silver (Ag), Copper Oxide (CuO) and Zinc Oxide (ZnO)

Silver (Ag) was a popular source of antimicrobial agent during the 20$^{th}$ century, when its demand reduced with the introduction of antibiotics. The increase of *methicillin-resistant* bacterium, in the forms of MRSA, MSSA and *E. coli* has just recently increased the demand of Ag within health care environments [64]. The high cost and difficult processing of consumer products has slowed the expansion of Ag as a source of microbial decomposition.

Silver ions presented the ability to decompose the cell wall and expose the cytoplasmic membrane of *Staphylococcus epidermis* (SE) and *E. coli* after 2 hours of incubation. Dark regions and grooves were present on the periphery of SE cells, and were increasingly apparent with incubation time, as presented in Figure 2.12 (C-I). After 4 hours of incubation time, a visible rupture was present in the cell wall and the cytoplasmic membrane was exposed, as presented in Figure 2.12(H&J).
Ag has permitted impressive antibacterial activity on MRSA, taking only 24 hours for a TiO$_2$-Ag composite to fully decompose bacteria on a porous layer [93, 94]. Composites of PP/Ag extruded fibers with 8 wt.% Ag added to the molten PP permitted excellent antimicrobial activity on SA and E. coli microbes [95]. Ag/PP composites had sustainable Ag$^{+}$ release properties, while still permitting ion release after 5 months. Ag$^{+}$ release properties depended on both the quantity of Ag and its chemical structure added to the PP matrix. Commercially available textile treatments within healthcare environments permitted significant antibacterial activity on MRSA [96]. Cliniweave™ treated PE proved to have the largest activity after 1 hour, where three commercially available Ag-based textiles failed to reduce bacterial presence. The presence of NPs of Ag was confirmed in the fiber structure by transmission electron microscopy (TEM). Antibacterial activity of CA nanofibers containing silver nitrate (AgNO$_3$) of 0.5 wt.% with a size of 21 nm permitted the growth of SA, E. coli, klebsiella pneumoniae (KP) and pseudomonas aeruginosa (PA) microbes after 18 hours [97, 98]. Microbial activity of Ag was increased by doping with nanopowders of TiO$_2$. Exposure to UVA irradiation increased the photocatalytic activity, therefore permitting an increasing activity against MRSA [83].

NPs of copper/oxide (CuO) have presented optical properties at low temperatures due to excitation absorption [99]. NPs of CuO applied to PE, nylon and cotton fabrics permitted good antimicrobial properties on microbes [100, 101]. CuO applied to cotton fabrics discoloured the fabric from white to brown [102]. CuO...
coated textiles had excellent coating retention and microbial activity after 20 cycles of laundering. The reduction of *E. coli* on textiles was dependent on the increasing quantity of CuO applied to surfaces. The antimicrobial reaction of Cu was further increased by combining with TiO$_2$-NPs. CuO deposited on thin films of TiO$_2$ presented antibacterial activity when no light was permitted [88]. When Cu and TiO$_2$ surfaces were illuminated, the photocatalytic ability of TiO$_2$ permitted an increase and further reduction of bacteria cells.

NPs of Zinc/oxide (ZnO) incorporate properties of an inorganic material with abilities including UV absorption, electrical conductivity, antimicrobial, and self-sterilisation [99, 103]. ZnO is a non-toxic oxide, producing good antimicrobial properties [100, 101]. NPs of ZnO applied to PET, nylon and cotton fabrics were reported to retain the fabric colour. Textiles coated with ZnO presented excellent retention of coating and microbial activity after 20 colour fastness cycles. Studies presented sensitivity and toxicity to biological life when exposed to small quantities of ZnO nanomaterials [62].

**2.2.5. Effect of Nanoparticles on Polymeric Integrity**

The decomposition and degradation of the polymer material substrate was considered the biggest obstacle of incorporation of NPs into or onto a surface structure. Photooxidation of polymers permitted a reduction of a materials transparency and mechanical properties [104]. The formation of non-volatile final products may require aggressive regeneration techniques, that can result in the deterioration of a coating of NPs on a surface [105]. The lifespan of a polymeric material may be distinguished by various environmental factors, such as solar radiation, temperature, thermal recycling, humidity, weather, pollutants, but most notably by UV light irradiation. Light wavelengths between the region of 280 to 315 nm were considered to reduce the integrity of HDPE polymers [106]. UV degradation was a factor of photolysis and oxidative reactions of the HDPE material. Polymer decomposition was present when subjected to solar and UV irradiation, when the polymer contained NPs [107]. HDPE surfaces coated with NPs can now be considered as a method of reducing the polymeric pollution by the decomposition of a polymer by photocatalytic reactions. For example, UV light has been reported to
accelerate photocatalytic degradation of poly (vinyl chloride) (PVC) coated with TiO$_2$ [108].

Composite materials of a polymer and TiO$_2$ from Degussa$^\text{TM}$ were investigated in the solid-phase for decomposition. The photodegradation of polystyrene (PS)/TiO$_2$ and PVC/TiO$_2$ has been reported to initiate in the presence of solar light [109-111], and composites of PE/TiO$_2$ were efficiently decomposed to H$_2$O and CO$_2$ after 100 hours of irradiation [112]. Increasing the concentration of TiO$_2$ on a polymer surface permitted reduction of the time required to decompose a polymeric material [112, 113]. The quantity of concentration of TiO$_2$ required for full decomposition of a polymer was substantial, where 1.5 wt.% of TiO$_2$ in a 50 ml solution of polymer was required. Mechanical integrity and surface degradation of polymers coated with NPs has not received much interest, as searched by the literature.

NPs of oxide nature were reported to increase the tensile strength of high density polyethylene (HDPE) polymers, and where multi-walled carbon nanotubes (MWCNT’s) act like a UV stabiliser. Polymers exhibited increasing stiffness after 100 hours of exposure to UV light, but then reduced slightly after 250 hours, which was also a common characteristic of plain HDPE [104, 114]. MWCNTs have been found to increase the stiffness of textiles [60, 61, 115], increase thermal stability [116], and electrical conductivity of HDPE [117].

The presence of a 35 µm film of TiO$_2$ on a PS substrate permitted a steady reduction of PS weight after 150 hours from the TiO$_2$/PS sample [118]. Molecular weight of samples of both TiO$_2$/PS and PS decreased 85% and 67% respectively over a period of 150 hours. The addition of a film of TiO$_2$ degraded at the TiO$_2$/PS interfacial region, which led to the formation of cavities around agglomerates of TiO$_2$. Surfaces of TiO$_2$ were diffused by a finite size for etching of the polymer matrix on the surface of the PS substrate.
2.2.6. *The Potential Hazardous Effects of Nanoparticles*

NPs bind readily with toxic pollutants and can be inhaled into the body. Here the NPs permit travel in the bloodstream and access to all of the vital organs. They can in theory travel throughout the body, into cells and cell nuclei, across the placenta and the blood-brain barrier, as demonstrated by in-vivo studies [4, 5]. The size of NPs permits penetration of human tissue more readily. The aspiration of nanotubes has been reported to create inflammation in the form of scarring and swelling, and a mutation of cells on the interior organs of animals [4, 5, 119]. NPs were also reported to be a serious environmental issue, where they were harmful when exposed to waste water, having a detrimental effect to plant life and forna. Studies highlight that TiO$_2$-NPs and ZnO were toxic to algae [120-122], water fleas [123, 124], and frogs [62].

NPs can penetrate the body through the skin, by absorption, inhalation through breathing and aspiration by swallowing. The National Institute for Occupational Safety and Health (NIOSH) outlined from a 28 day study on mice [125], that the inhalation of MWCNT’s exposed in an environment is considered more toxic than the aspiration by swallowing of MWCNT’s. Dispersive applications can be reduced by altering the strength of toxicity of degradation products. Influencing the size of NPs that are not inherently dispersive, due to tear, wear and corrosion is important in limiting associated hazards [126].

As nanotechnology is a more recent area of technology, information is limited in the scope of a life-cycle of NPs. Workers handling NPs should abide to material safety data sheets (MSDS), and wear suitable PPE at all times. No MSDS data sheet currently accounts for the size effect of the extraordinary SA/V ratio of the same chemical species. While NPs should be disposed of according to hazardous chemical waste guidelines [127], much research is required in the area of NPs toxicity and the effects on human, animal, and plant life. A lack of knowledge exists in the cosmetics industry, where the use of NPs into the structure of moisturisers and creams is penetrating the industry. The American Association for Cancer Research (AACR) reported the future carcinogenic effect of NPs [128], and the requirement of further research in this area. The modification of MWCNT has been reported to reduce the toxicity [129].
The National Science Foundation have estimated that up to 2007, close to US$70 billion worth of nanotechnology-enabled products were sold in the U.S.A annually, with an expected increase in that estimate [130]. As of 2012, there exists no obligation for manufacturers to label products that contain NPs, with a severe lack of voluntary information containing these elements made available to consumers. Sunscreens most likely contain TiO$_2$-NPs or ZnO, due to abilities to shield UV light [131]. It has been reported that no penetration of such NPs through healthy and intact skin exists [132], while there exists no available data reporting the bodily reactions when damaged or broken skin is penetrated by NPs.

A containment strategy of NPs can be adopted, where the exposure to the environment is reduced by incorporating exceptionally low quantities of NPs to products for consumer application. The NPs must have reliable adherence to the surface or matrix of the product, while still permitting efficient functional abilities. Through efficient distribution of NPs, the quantity of NPs applied on a textile product is substantially reduced, while still permitting effective antimicrobial abilities.

2.3. Incorporation of Nanoparticles to Textile Substrates

Nanotechnology is considered a novel approach to instil self-cleaning functions into textile materials. A textile that with abilities to remove a coffee stain by water, or prevent microbial penetration on a gown or drape would generate excitement in the textile and clothing industry. Popular areas of textile research in the nanotechnology sector are listed in Table 2.9:
Table 2.9 Areas of nanotechnology research and desired properties in the T&C industry.  
Reproduced from reference [133]

<table>
<thead>
<tr>
<th>Research Area</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional Finishes</td>
<td>Wrinkle, stain, static resistant fabrics</td>
</tr>
<tr>
<td>Protection</td>
<td>Chemical and biological threats</td>
</tr>
<tr>
<td>Spinning</td>
<td>Nanofiber and yarn</td>
</tr>
<tr>
<td>Smart and Medical</td>
<td>Climate control, antimicrobial</td>
</tr>
<tr>
<td>Composites</td>
<td>Polymer decomposition, Superior mechanical properties and performance</td>
</tr>
</tbody>
</table>

Incorporation of NPs into textiles enhances a textiles ability to protect from microbial and fungicidal habitation. An efficient antimicrobial textile permits the following characteristics [133]:

- Reduce cross infection caused by pathogenic microorganisms
- Control the infestation of microbes
- Arrest metabolism in microbes in order to reduce the formation of odour
- Safeguard the textile material from staining, discoloration and retain quality

Antimicrobial fabrics can prevent microbial growth by “passively” inhibiting the growth with these fabrics, for example, lamb’s wool; or it can “actively” prevent growth by treating the fabric surfaces with NPs that inherit antimicrobial properties. Such properties can kill and/or prevent the growth of microbes on fabrics [47].

NPs can be added to textiles in several ways, including coating or incorporation into the fiber during extrusion. Techniques applied to maximise the efficiency of adherence of NPs to textile surfaces by coating or incorporation techniques have been adopted from numerous sectors. Dip- and spin-coating are popular techniques applied in the electronics industry to develop thin films. Techniques commonly employed in the incorporation of NPs into textiles are presented in Table 2.10.
Table 2.10 NPs incorporation techniques into polymeric materials. Adapted from [134, 135] [36, 105, 136-149] [150-160]

<table>
<thead>
<tr>
<th>Technique</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dip-coating</td>
<td>Textile immersion in aqueous solution, then cured</td>
</tr>
<tr>
<td>Padding</td>
<td>Pad containing wet solution of NPs is pressed onto a textile surface</td>
</tr>
<tr>
<td>Spin-coating</td>
<td>Textile rotated and disperses NPs over the surface</td>
</tr>
<tr>
<td>Sonochemistry</td>
<td>Ultrasonic vibration of NPs to textile</td>
</tr>
<tr>
<td>MW, RF and UV Irradiation treatment</td>
<td>Surface tension activation for increased adhesion of coatings of NPs</td>
</tr>
<tr>
<td>Binder Assistance</td>
<td>Chemicals that assist to reduce the process temperature</td>
</tr>
<tr>
<td>Electrohydrodynamic Spraying</td>
<td>Fine dispersion of droplets on surface for thin film formation</td>
</tr>
<tr>
<td>Polymer Spinning</td>
<td>NP added to polymer mix or molten and extruded by a fiber extruder (spinneret)</td>
</tr>
<tr>
<td>Electrospinning</td>
<td>Fiber extrusion by electrostatic force</td>
</tr>
</tbody>
</table>

2.3.1. Surface Coating Techniques of Nanoparticles to Textiles

Direct coating of solutions of NPs to textile surfaces have been a very popular technique with researchers. Several coating techniques have been attempted and tested, where dip-, spin- coating and padding of textiles by an aqueous solution of NPs has been employed. Sonochemistry was a novel technique applied in the coating of thin films on textile surfaces. Chemicals structures incorporating sol-gel and binding solutions and surface tension activation by plasma treatments were employed to increase the surface adherence between a textile and NP.

Direct Dip-Coating and Sol-Gel Activation

Dip-coating is a popular technique in the application of a uniform homogeneous film on an uneven material surface. This involves immersing the material into an aqueous solution containing NPs, where the solution is then deposited on the material surface by drying in ambient conditions, or direct application of heat as presented in Figure 2.13 [134]. The excess solution on the surface of the material is then drained by drip-drying before the solvent evaporates, leaving a thin film behind.
The concept of self-cleaning textiles was first achieved by applying a solution of TiO$_2$ sol-gel to cotton fabrics by a *dip-coating* procedure [135], permitting a transparent thin film coating on the textile surface. Sol-gel is a wet chemical technique employed in material and ceramic engineering. A colloidal suspension acts as the sol and a precursor mostly consisting of polymers act as the gel [134]. Sol-gel films require high processing temperatures for efficient crystallisation of TiO$_2$ on a fiber surface [136].

Cotton/TiO$_2$ fabrics were prepared by *dip-coating* in a solution of TiO$_2$ for 2 minutes, then cured for 2 minutes in ambient conditions, rinsed with water, and then dried at high temperature for 8 minutes [137]. Cotton/TiO$_2$ permitted an 89% reduction of *E. coli.*, with an 81% reduction of *E. coli* cells when the fabric was laundered for 50 cycles. The strong interaction between NPs and cotton fibers was initiated by the lodging of NPs into interstitial regions in the fiber matrix. Research highlights differing outcomes to coatings produced by the *dip-coating* technique [138]. Short contact times between cotton fibres and bacteria permitted inactivity of *SA* and *E. coli.* cells. The stability of a sol-gel coating was presented after laundering cycles, where water rinsing took place at 65°C for 15 minutes. Cotton, PE and Poly/cotton textiles have increasing an UV protection factor (UPF) when coated with ZnO [139], where PE coated textiles have the largest increase in UPF. Textiles
treated with ZnO, and aluminium/ZnO has less moisture than untreated textiles. The technique of employing sol-gel as part of a dip-coating procedure has been extended to PET textiles [140]. Further development is required to increase the absorption range of this coating into the visible range (390–750 nm) which would improve the textiles photodestruction of soilage and bacteria [141, 142].

The addition of sol-gels applied by dip-coating processes increase the adhesion of coating of TiO₂ to PET textiles, where high photocatalytic activity against a decomposing air contaminant is permitted. Surface topography of PET/TiO₂ coated textile fibers are presented in Figure 2.14. A thick homogeneous coating of TiO₂-NPs is evident on the fiber surface, Figure 2.14(a). A visibly large presence of agglomeration of NPs and the poor efficiency of SA/V ratio is observed, as presented in Figure 2.14(b).

![Figure 2.14 SEM images of TiO₂ NPs bonded on a fibre of nonwoven PE textile; fully coated fiber (a), and large presence of agglomeration of NPs [161].](image)
The elimination of H$_2$S from polluted air by PET and CA textiles requires five repetitions of dip-coating in solution of TiO$_2$, where textiles are then dried at 50°C after each layer of coating [105]. Characterisation by imaging shows a homogenous distribution of the coating of TiO$_2$ sol-gel on the PET and CA surfaces. Compared to conventional methods, the TiO$_2$/PET material has similar photocatalytic conversion of H$_2$S, and permits a lighter and cheaper material. The adhesion of the catalyst to the polymer surface must be enhanced for this method to be considered a viable option in the production of photocatalytic materials.

**Application of Coating by Padding Technique**

The *padding technique* is an ideal method of coating textiles at room temperature and pressure, but it is a highly inefficient procedure. It involves application of a coating by *padding* a textile with a sponge immersed in a solution containing NPs [143]. A coating of NPs of Ag applied to a PE textile permits good antimicrobial effects on *SA* and *KP* [143]. There are no results published to prove the long term bioactivity of the textile when subjected to cycles of laundering. Textiles with low quantities of applied Ag retain good antibacterial activity on *SA*, but fail to decompose *KP*. Employing the *padding* technique, changing the NPs from Ag to TiO$_2$ presents similar outcomes [36]. Preparation of PET/TiO$_2$ surfaces display good distribution and dispersion of NPs over fiber surfaces, where excellent shielding performance from UV light also exists. The *padding* technique can be employed to activate cotton fabrics with commercially available photocatalytic material, known as Actigard™ AM-87 [144]. Fabrics are padded until wet, and then dried at 80°C for 5 minutes, where they are finally cured at 100°C for 150 seconds. Activity against *SA* and *E. coli* was permitted, with a marginal decrease of tensile strength, roughness, elongation at the break and whiteness index.

Cotton fabrics pressed by *padding* with an aqueous sol process of TiO$_2$ have a visible presence of TiO$_2$-NPs on the surface, as presented in Figure 2.15 [145]. The cotton was immersed in TiO$_2$, pressed by *padding* at pressure, heated, cured and finally washed in hot water for removal of loose NPs. Poor dispersion of NPs and densely populated areas of coating of TiO$_2$ on the cotton surface is noted. Agglomerates of NPs have increasing population in the margins of the fibres, when
compared to exposed fiber surfaces. The cotton fabric has promising photocatalytic activity and antibacterial activity.

Figure 2.15 SEM images of untreated cotton fabric (a), and TiO₂ treated cotton fabric (b) [145].
**Spin-coating**

Spin-coating is a technique primarily employed to develop thin films in the electronics sector. It involves the placement of a solution into the centre of a surface substrate. The substrate is then spun, where the solution spreads out over the surface due to rotational forces, as illustrated in Figure 2.16 [134]. Spin-coating is highly dependent on the spin speed, spin time, angular speed and the viscosity of the solution.

![Figure 2.16 Schematic illustration of the spin-coating process, solution deposition on textile surface (a), spinning surface spreads solution over surface (b). Reproduced from reference [134]](image)

Photocatalytic response of NPs has been achieved for ratios of sol-gel derived hybrid films applied to poly(methyl methacrylate) (PMMA) substrates [146]. Transparent hybrid films of TiO$_2$/PDMS applied to PMMA substrates by spin-coating and sol-gel solutions permitted good photocatalytic activity. Low temperature crystallisation was necessary to exploit the photocatalytic properties of sol-gel films of TiO$_2$ deposited on thermally sensitive substrates, such as polymers. Ti sols were prepared in basic conditions [162], and then deposited by spin-coating as thin films onto polymer substrates at room temperature. UV/visible transmission spectra of thin films from sols were refluxed for 1 hour and reported to be 10% weaker than that of bare polymer surfaces. This poor optical quality was a factor of the non-uniform and inhomogeneous thin film surface presented. Surface finishing of films that were refluxed for 6 hours were of increased quality, as presented by the SEM image in Figure 2.17. Good crystallisation achieved from the basic sols permitted the deposition of films of TiO$_2$ on polymer surfaces at room temperature.
Sonochemistry

Sonochemistry is a method employed to deposit thin films on various materials through ultrasonic radiation. A special purpose machine can be employed to sonochemically assist the coating of NPs to textile fabrics [102]. Fabric is transferred through two ultrasonically vibrating plates immersed in a solution, as illustrated in Figure 2.18 [102]. Acoustic cavitation drives NPs at high velocities into the fiber surface, which permits a homogeneous film on the surface.

![Figure 2.17 SEM images of films deposited from a sol refluxed for 6 h [162].](image)

![Figure 2.18 Schematic illustration of textile coating by sonochemistry. Reproduced from [102]](image)
Sonochemically coated textiles permit stable and homogeneous coatings, as well as strong retention of microbial properties after 20 cycles of laundering [102]. Employing CuO or ZnO, *sonochemistry* can produce a continuous coating of cotton for as much as 50 metres of fabric. These coatings can be optimised by altering the concentration of the solution, or varying the speed of the fabric through the plates. CuO permits good antimicrobial properties against *E. coli*, while it changes the fabric colour from white to brown after coating.

MgO and Al₂O₃ loading of 1 wt.% coated by *sonochemistry* on cotton bandages permit good antimicrobial activity [147], and retain colour after sonication. Metal oxides added to the cotton without the presence of sonication had no resistance to microbes. Tensile mechanical properties of cotton bandages with MgO and Al₂O₃ on surfaces have a brittle fracture (10%) after sonication, but no visible damage to the fabrics was noted. The fabrics are tested in by cycles of laundering, where no presence of NPs are recorded in the wash water, therefore proving good adherence of the NPs to the cotton, as presented by the images in Figure 2.19.

![Figure 2.19 SEM images of CuO treated cotton bandage, after 10 min. of reaction (a), after 40 min of reaction (b), after 40 min of reaction with precursor addition (c), uncoated cotton bandage (d), and cotton bandage immersed in CuO without sonication (e) [147].](image-url)
Plasma Treatment

Plasma is a partially ionised gas, described as an electrically neutral medium of positive and negative particles. A radio frequency potential (RF) applied to a gas at reduced pressure is accompanied by a glow discharge [148]. Plasma treatment increases the surface tension of polymeric materials, modifying its surface chemistry, and increasing the polar interaction with an adhesive [148, 149]. Upon activation of textile surfaces with plasma treatment, they can be coated by dip-, spin-coated or padded in an aqueous solution of NPs. Low temperature plasma has a positive effect on the adherence of NPs to a surface. Coatings applied with the aid of plasma treatment achieved on metallic alloys present retention and good adherence of coating [151].

Low density polyethylene (LDPE), PP and PE foils exposed to low-pressure microwave (MW) plasma was achieved using an oxygen and hydrogen pressure of 3 Pa. Adhesion was measured between the polymer and a known adhesive by Pull-Off tests. Treating LDPE by oxygen and hydrogen plasma increased the Pull-Off strength by a factor of twenty after 6 seconds, while an extended treatment of 30 minutes presented a decay of the bond strength. A 15 minute treatment of PP permitted an increase of the bond strength by a factor of seven, while PE had no increase in bond strength after this duration of time. Plasma treating with oxygen presented a correlation between bond strength and the polar part of the surface tension for tested polymers. There exists no significant relationship between bond strength and polar surface for plasma treated polymers with hydrogen. Textiles treated with methods incorporating RF and MW plasma, and vacuum-UV irradiation has been achieved to produce textiles coated with NPs [150, 163, 164]. PET and PP textiles were loaded with Ag, firstly treating by RF-plasma and UV irradiation, then immersing the textile in concentrations of AgNO₃ solution. RF-plasma treated textiles required low quantities of Ag loading to decompose E. coli growth.

Plasma treatment can increase adhesion of NPs to PET fibers. PET was prepared by treating with low temperature plasma (LTP), and applying a TiO₂ aqueous sol-gel process at 60°C [140]. Parameters of LTP exposure time and discharge were set at a temperature just below the T_m of the textiles. Textiles were tested for surface alteration, with the outcomes presented in Figure 2.20. Plasma
treatment initiated etching on the polymer surface, Figure 2.20(b), where a clear presence of granules and ripple-like structures was noted. After plasma treatment, there existed a visible presence of TiO₂ surface layers, Figure 2.20(c&d). Increased roughness was observed as the fundamental characteristic for the high deposition of TiO₂-NPs on the polymer surface [140, 165].

Figure 2.20 SEM images of original polyester filament (a), oxygen plasma pre-treated polyester filament (b), TiO₂ coated polyester filament pre-treated with oxygen plasma (c), and TiO₂ coated polyester filament pre-treated with oxygen plasma at a high resolution (d) [140].

PET textiles coated with TiO₂ and prepared with surface modification by plasma treatment have excellent killing activity against S.4 when subjected to UV irradiation for 5 hours. Cycles of laundering permitted high durability of TiO₂ to PET textiles, with minimal reduction of antimicrobial activity when compared to PET/TiO₂ textiles that were not laundered. The surface changes on PET textiles after plasma treatment lead to a loss of the textiles mechanical properties [140]. Mechanical testing of textiles treated by plasma should be achieved to verify the stability of PET. Cotton fibers were treated by way of RF and MW plasma, and
vacuum-UV irradiation [150]. Cotton samples that were UV irradiated and then dip-coated in TiO₂ Degussa™ had good activity during discoloration of wine and coffee stains under daylight irradiation.

Loading of TiO₂-NPs by wet chemical techniques has been achieved on surfaces pre-treated by RF and MW plasma, and UV irradiation. PET and wool polyamide textiles were dip-coated in a variation of TiO₂ solutions, with good adherence of NPs and retention of photocatalytic abilities after laundering [163]. Wool-polyamide presented best photocatalytic activity, and retention after laundering. A solar simulated light was sufficient to self-clean wine and coffee stains. Stained PET and wool-polyamide textiles before and after light irradiation of 24 hours are presented Figure 2.23.

![Figure 2.21 Discolouration of red wine stains on the TiO₂ loaded samples where: (1) before; (2) After light irradiation for, PET textile (a), and wool-polyamide (b) [163].](image)

*Plasma treatment* of PU material coated with NPs of Ag permitted decomposition of *E. coli* as it came in contact with the surface, and also inhibited further microbe adhesion [155]. Ag was coated on the polymer films by sonochemistry. *Plasma treatment* was achieved in a reaction chamber with a microwave (MW) generator. The highest observed activity of coated PU was achieved from films with small isolated agglomerates of Ag on the surface, which was initiated at low plating times of 120 seconds. Surface modification by *plasma treatment* of substrates of PU permitted good adherence of coatings of Ag on its surface. A tape test quantified the adhesion of the PU/Ag composite, with little to no effect on the Ag coatings.
Application of Binders

Binders are chemicals used to assist the adherence of NPs to material surfaces, which is achieved by reducing the sintering temperatures employed in the creation of films. Reducing the processing temperature of coatings permits a broader range of NPs that can be employed, and prevents loss of antibacterial abilities on application to the surface. The stability of silicon dioxide (SiO$_2$) and photocatalytic stability of TiO$_2$ presents a suitable binder material [136]. TiO$_2$/SiO$_2$ can be applied to cotton substrates by dip-coating at 100°C, then dried in ambient conditions and cured at 100°C for 1 hour. A translucent coating thickness of 25 nm is present on the cotton surface where content of 5.8% of TiO$_2$ is detected by EDS. NPs on the fiber surface are poorly dispersed over the SiO$_2$ layer, where embedding is initiated in the thin film of the cured solution of SiO$_2$, and not in the cotton substrate. Irradiation of solar light on the TiO$_2$/SiO$_2$-cotton enables good photocatalytic activity, and can completely discolor red wine stains after 24 hours of irradiation, as presented in Figure 2.22.

Fluoropolymer’s are binders of fluorocarbon polymer with good stability that are commonly used for lining manufactured metal parts. Thin films of TiO$_2$ can be applied to polymer substrates by preparation of a sol-gel solution of TiO$_2$ and binder of fluoropolymer resin [152]. A highly concentrated (90%) film of TiO$_2$ is applied to the substrate and permits a homogeneous coating of NPs. UV irradiation of the surface initiates small cracks to the binder, which is attributed to the decomposition of the binding agent during treatment. Binders that are treated by UV irradiation can increase and permit long term photocatalytic stability of the binder. Photocatalytic
films on polymer substrates have good adherence, high photocatalytic activity and stability when irradiated. Impregnating woven and knitted fabrics (100% Cotton and 45/55% poly/cotton) with TiO$_2$ can be achieved using a two-step method of application of the binder [153, 154]. Binders are applied to fabric surfaces twice, firstly by using a spray-gun and secondly by a padding method, where excess solution is squeezed with a pad. Good dispersion on the fibre surface is present, which permits excellent antimicrobial activity against SA and KP. Cotton fabrics coated with TiO$_2$ have the ability to decompose wine stains, cosmetics, perspiration and coffee after 24 hours of UV irradiation time.

**Fibre Extrusion of Nanocomposite by Polymer Spinning**

Mixing NPs with textile powders or molten before fibres are extruded is a popular method in the production of nanocomposites with antimicrobial properties. Textile fibres are fabricated by polymer spinning, which is achieved by applying multi-holed device known as a spinneret. This method creates a homogeneous distribution of NPs throughout the fibre matrix and increases adherence of the NPs to the fibres. Large quantities of NPs are wasted incorporating this technique, as the photocatalytic properties of the NPs are only active against microbes at the fiber surface [156, 157]. Nanocomposite materials should have mechanical properties for the applications they are required, retain their fabric abilities and exhibit high antimicrobial stability [166]. Poor distribution of NPs within a nanocomposite could reduce the mechanical properties of a fibre.

NPs of TiO$_2$/Ag mixed with PVC powder can form a fiber nanocomposite [158], with low agglomeration of NPs and homogeneous distribution in the organic matrix. Antimicrobial activity of PVC/TiO$_2$-Ag fibers has increasing activity on SA compared to activity on *E. coli*. Fibers of PP/Ag are prepared by spinning through a spinneret and then dried for 2 hours at 100°C in a vacuum drier [167]. Good dispersion of Ag is present in the fibre matrix, with excellent antibacterial activity at the surface, while fibres containing Ag within the core-part of the fiber has poor activity. The stability of NPs inside a matrix has been investigated, by producing nanocomposites of Ag/silica extruded with PP by spinning [93]. The forming of Ag inside the silica pores reduces the instability of the NPs. The NPs stored in the
porous matrix present stability against thermal reduction and photoreduction reactions. The nanocomposite of Ag/silica permits good antimicrobial activity and retains its whiteness.

Ag loaded in molten PP is spun to form fiber nanocomposites, as highlighted in Figure 2.23. A fine dispersion of NPs that have a specific surface area of 0.78 m²/g was present in the PP matrix [168]. Minimal exposure of NPs to the outer fiber surface exists, where the majority are inefficiently dispersed within the fiber matrix.

![Figure 2.23 SEM imaging of Ag/PP nanocomposites, 2 wt.% (a), 4 wt.% (b), 8 wt.% (c), Ag in PP matrix (Surface Area - 0.78 m²/g) [168].](image)

A surface of nanocomposite fiber that incorporates NPs of Ag with a surface area of 2.5 m²/g is presented in Figure 2.24. The fibers present large agglomerates of Ag within the PP matrix, as highlighted. Large agglomerates greatly reduce the efficiency of a NPs SA/V capability, and the mechanical properties of a fiber, including the strength, elasticity and comfort of the fiber.

![Figure 2.24 SEM image of Ag/PP nanocomposites containing Ag particles with surface area of 2.5 m²/g [168].](image)
Alginate fibres are mainly employed as a thickener in food stuffs. They are fabricated from alginic acid or salts of the fibrous parts from cell walls of seaweed. PVA has replaced alginate fibres in all but one application, where a haemostat which is a wound dressing used for assisting blood to clot [15]. Advantages of alginate fibres include excellent biocompatibility, non-toxicity and potential bioactivity. Nanocomposite fibres are produced by placing prepared alginate fibres in a treatment bath comprising of a solution of Ag [166]. The fibres present a smooth substrate and efficient blend of homogeneity between the alginate and NPs of Ag. The fibres have an excellent reduction rate of SA, and retain mechanical properties for both wet and dry elongation. PET and a combination of polysaccharide alginate with TiO$_2$ can be spun to form a nanocomposite fibre [166, 169]. These fibers permit excellent adherence, where the fiber has good antimicrobial and UV protection after 5 cycles of laundering.

Polyacrylonitrile (PAN) fibres doped in 0.5 wt.% of Ag incorporate the *spinning* method, and retain minimal quantities of Ag [170]. After 60 days of flushing with distilled water, the content of Ag on the fibre decreases from 0.19% to 0.1%, where a distinct lack of adherence to the fibre exists. NPs of Ag are larger than the pores in the PAN fibres, with NPs dislodged by the dissolution of the water permeating through the pores. Ag depleted rapidly during the laundering process, however there still was a presence of antimicrobial activity of the fibre on both *E. coli* and *SA*.

*Electrohydrodynamic Spraying and Extrusion of Fibers*

An electrohydrodynamic atomiser is a low-energy, low-cost and a single-step process technology, as presented by the schematic illustration in Figure 2.25 [159]. The formation of small self-dispersing droplets in the process of *electrohydrodynamic spraying* is an advantage in engineering when applying surface coatings, electro-scrubbing and thin-film production. Field induced liquids are moved and broken into droplets by acting together with external electric fields when flowing out of a capillary nozzle. The size of droplets can be varied from micrometres to nanometres by controlling the flow rate of particle suspension and the current supplied to the capillary nozzle [159]. With its small apparatus, accurate
control of fabrication, dispersion and deposition, *electrospraying* is an increasingly important technique in the field of nanoscience and nanotechnology research [160].

![Figure 2.25 Schematic illustration of an electrohydrodynamic atomiser. Reproduced from reference [159].](image)

*Electrohydrodynamic spraying* can be utilised for the following purposes [159, 160]:

- Applying thin solid films for use in manufacturing micro- and nanoelectromechanical systems (MEMS or NEMS).
- Semiconducting, insulating or conducting layers in microelectronic devices.
- Altering surface properties of mechanical elements.
- Micro- and nano-particle production as a powder in ceramic coatings, production of emulsion or paint as employed in the cosmetic or pharmaceutical industry.
- Process of encapsulating liquid droplets, solid particles or a gaseous bubble as a core material within a shell of another material.
- Use of spray forming to produce a thick coating by deposition of semi-solid droplets of a material onto a substrate layer-by-layer.
- The fabrication and advancement in modern technology of materials for cosmetic, medicine and food industries in biological processing.
Electrospinning is a combination of electrospraying and solution dry-spinning methods. It is the process of placing a polymer solution into a capillary-tube containing a millimetre-sized nozzle and subjecting it to multiple kilovolts of electrical fields [171]. The polymer which is under an applied electrostatic force is ejected from the capillary nozzle and deposited to a collector, which acts as a ground to the electric charges. Advantages of electrospinning are the high SA/V, small pore size and high porosity. Nanocomposites of PVA can be prepared by electrospinning PVA/silver nitrate (AgNaO₃) aqueous solutions [171], then heat treating at 155°C to finish. UV irradiation of NPs of Ag can increase size by 0.4 nm to 6.3 nm. Heat treating the electrospun solutions conserves the web structure of the nanofibers in water, but a change of the fibre colour to yellow is also permitted. The PVA/AgNO₃ nanofibers exhibit a very strong antimicrobial activity, reducing the presence of SA and KP by 99.9% after 18 hours of incubation. A biodegradable poly(1-lactide) (PLA) and Ag nanofiber is produced using the electrospinning method, and reduces SA by 98.5%, and E. coli by 94.2% after 12 hours [172]. Characterisation outcomes of nanofiber using imaging by SEM and EDs are presented in Figure 2.26. A homogeneous distribution of NPs of Ag in the PLA fiber matrix is permitted, where poor exposure of NPs to the outer fiber surface is also observed.

Nanofibers of PVC, PSU or nylon material containing TiO₂ are produced by electrospinning [173, 174]. TiO₂ of 3 wt.% is calculated from the solution and suspension concentrations and flow rates. The outcomes of electrospun nanofibers are presented in Figure 2.27. A dense deposit of NPs is clearly visible on the fiber substrate. NPs that did not penetrate the fabric are deposited on the fiber surface.
Poor dispersion of NPs, and a reduced adherence to the fiber surfaces is observed. Fibers processed by this method present poor adherence of NPs for multiple colour fastness cycles.

Figure 2.27 SEM images of TiO$_2$ deposited by electrospinning with 0.06 wt.% concentration of TiO$_2$, PVC nanofibers (a), polyethersulfone (PSU) nanofibers (b), and nylon nanofibers (c) [173].

2.4. Contact, Adhesion and Embedding of Particles into a Matrix

The durability of a compound material when subjected to abrasive instances is reliant on the adhesion between the substrate and coating. A combination of an adhering substrate and an adherent coating is known as an adhering system. Poor adhesion within the adhering system permits increasing exposure to humidity, abrasion, discolouration and corrosion, where deterioration of the substrate is initiated at an accelerated rate. The measurement of adhesion can be categorised as a method for [7, 175];

- Assessment of the preparation of a substrate, where conditions are optimised to increase adhesion strength.
- Examination of acceptable parts or products with good adhesive strength.
- Understanding the mechanisms of adhesion.

The term “basic adhesion” signifies the interfacial properties of the interfacial bond strength. Basic adhesion is considered to consist of electrostatic, chemical and/or van der Waals type interaction forces. A number of factors are involved in the creation and destruction of a bond. The interfacial chemistry is critical during the creation of the bond [7, 8]. The term “basic adhesion” is irrelative to a non-homogenous coating on an interface of a substrate. Therefore the coating in this study has an undefined interface.
2.4.1. Characteristics of Adhesion

Adhesion has a significant role in science and technology, where work is undertaken in areas such as: material science; tribology; nanotechnology; and biochemistry. The standard terminology for adhesion of a compound is split into two distinct terms. The first term is the adherend, which is a solid substrate that a material will adhere to. The second is termed an adherate, which adheres to the adherend. The two substrates are held together by the interfacial forces of attraction, through the interactions of atoms, ions and molecules in the two surfaces [176, 177]. The adhesion between two surfaces permits either chemical or physical bonding. Chemical bonding initiates the direct interlinking between adhesive and substrate molecules in the two substrates. This is achieved by the formation of primary and secondary bonds. Physical bonding between the two surfaces is initiated by mechanical interlocking and penetration of the adherate into the solid phase by diffusion. Physical bonding may also be initiated by forces of physical absorption between the adherate molecules and the substrate molecules [7, 178].

The quantitative and qualitative measurements of adhesion between a substrate and adherate provides a method of achieving acceptable and unacceptable specifications of an adhered system that has been engineered [179]. The measurements will determine the specifications for an optimised process, and set the standards for a quality control process. The measurement of adhesion can be quantified experimentally by work of surface detachment or separation of the adhering system [180]. It is this type of practical adhesion that is relevant in the engineering of an adhering system.

The separation of an adhering system can initiate at the interface, or the interfacial region, or in the bulk of the weaker adhering phase. The separation is known as the cohesive strength of that bulk phase. An interfacial phase is predicted as a point of weakness in an adhering phase [7, 180]. In the presence of oil or interfacial cracks on the surface, or excess moisture, a failure of the adherend system can initiate. An interfacial region permits rise to the occurrence of additional interfacial regions. Mechanical failure of the adhering system can initiate at any of the interfaces, and between the two bulk materials [177]. If failure of the adhering system initiates at an interface or in any interfacial region, the measured adhesion is
referred to as “practical adhesion”. Studies contradict this assumption, where the existence of interfacial failure in a bond where the molecular interaction between the adherate and adherend has initiated is thought to permit failure. What is thought to be interfacial failure, is really a fracture of a poor boundary layer [180]. Where practical adhesion does not vary directly with changes in basic adhesion, then the basic adhesion can only be achieved with the aid of quantitative techniques of practical adhesion [177]. In the case of applying different practical techniques to quantify values, the outcomes may not directly correlate. A simple correlation between practical and basic adhesion might not be achieved.

2.4.2. Contact Mechanics Theory

Creating a new surface in a liquid or solid is achieved by breaking the bonds that ensure the cohesion of that condensed phase. This requires a particular quantity of energy, either by work and/or heat that is measured per unit area of the created surface. The work or heat required to reversibly and isothermally create a unit area of new surface is called the surface energy, \( \gamma \) (J/m\(^2\)) [181]. The science of particle adhesion relies on the interaction mechanisms and the mechanical properties that exist between the material surfaces in contact [181]. Van der Waals and electrostatic interactions from electromagnetic interactions that can reside on particles generate stresses that result in deformations. Small particles permit the production of large strains, initiating yielding and plastic deformations. It is also possible that the particle can become entirely consumed by the substrate. The adhesion forces between a particle and a substrate create stresses. The sphericity and fast oxidation of metal particles when exposed to atmosphere, are a few other factors that may complicate the adhesion mechanism [182].
The adhesion of elastic bodies in contact is extended from the Hertz theory by Johnson, Kendall and Roberts (JKR) and Derjaguin, Muller and Toporov (DMT) [183], where the respective theories for displacement, δ embedding force, P and Pull-Off force, P' are presented in Table 2.11.

Table 2.11 Contact mechanics theories for particles in contact with a surface. Reproduced from reference [181-191]

<table>
<thead>
<tr>
<th>Theory</th>
<th>Displacement (δ)</th>
<th>Embedding Force (P)</th>
<th>Pull-Off Force (P_{pull-off})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hertz</td>
<td>δ = a^2 / R</td>
<td>P_o = h_w / 8πZ_o^2 R</td>
<td>None</td>
</tr>
<tr>
<td>JKR</td>
<td>δ_{JKR} = a^2 / R - 2 / 3 πaW_o / E</td>
<td>P_{JKR} = 4Ea^2 / 3R - (8πa^2W_oE)^{1/2}</td>
<td>P'_{JKR} = -3/2 W_AπR</td>
</tr>
<tr>
<td>DMT</td>
<td>δ_{DMT} = a^2 / R</td>
<td>P_{DMT} = 4Ea^2 / 3R - 2πRW_o</td>
<td>P'_{DMT} = 2πW_AR</td>
</tr>
</tbody>
</table>

This particular area of science now known as “Contact Mechanics,” considers the effect of adhesion in the contact area. Here the contact of a sphere initiates on a plane, where Hertz assumed a hemispherical pressure distribution in the contact area. The Hertzian indentor relates the contact radius, a to the surface-force generated load, P_o and the surface radius, R of the particle by [184]:

\[ a^3 = \frac{3}{4} P_o \frac{1-v^2}{E} R \quad (2-2) \]

Where, E is the elastic modulus between the systems:

\[ E = \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2} \quad (2-3) \]

And, E_1, E_2, \nu_1 and \nu_2 are the elastic moduli and Poisson’s ratio of the contacting materials, respectively. Assuming that the forces are a consequence of van der Waals interactions, then:

\[ P_o = \frac{h_w}{8πZ_o} R \quad (2-4) \]

Where, h_w is the Lifshitz-van der Waals constant for the materials in contact, and Z_o is the equilibrium separation distance between the particle and the substrate.
The theory of JKR recognises that both compressive and tensile forces contribute to the size of the contact radius between the particle and the substrate. The theory assumes that the adhesion-induced deformations are fully-elastic, where \( \delta \) the elastic displacement is given by:

\[
\delta_{JKR} = \frac{a^2}{R} - \frac{2}{3} \frac{n\alpha \gamma_a}{\gamma_s} \frac{1}{E}
\]  

(2-5)

The deformations can be calculated from three terms, as presented in Figure 2.28:

1. the surface energy of the particle and surface,
2. the elastically stored energy from creating the contact zone,
3. the mechanical potential energy contributed by the applied load.

The JKR contact radius is given by [184, 185]:

\[
d_{JKR}^3 = \frac{PR}{K} 1 + \frac{3\pi \gamma_a R}{p} + 2\frac{3\pi \gamma_a R}{p} + \frac{3\pi \gamma_a R}{p}^2 1/2
\]  

(2-6)

Where:

\[
K = \frac{4}{3} \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2}
\]  

(2-7)

Manipulating Eq.2-6, for an externally applied load \( P_{JKR} \):

\[
P_{JKR} = \frac{4Ea^3}{3R} - (8\pi a^3 \gamma_a E)^{1/2}
\]  

(2-8)

where \( \gamma_a \) is the work of adhesion which is defined as [184, 185]:

\[
\gamma_a = \gamma_p + \gamma_s - \gamma_{ps}
\]  

(2-9)
\(\gamma_p\) and \(\gamma_s\) are the surface energies of the particle and the substrate, respectively, and \(\gamma_{ps}\) is the interfacial energy:

\[
\gamma_{ps} = \gamma_p + \gamma_s - 2 \gamma_p \gamma_s^{1/2}
\]

(2-10)

If no load is applied, then Eq.2-6 will reduce to:

\[
a_0^{3\text{ JKR}} = \frac{6\pi\omega_a R^2}{k}
\]

(2-11)

and the elastic displacement is given as:

\[
\delta_{\text{JKR}} = -\frac{a^2}{3R}
\]

(2-12)

The JKR model assumes that the area of contact remains small compared to the dimensions of the contacting bodies. There are no long-range interactions considered in this theory. Only interactions within the contact zone are considered, where the theory is proved applicable to soft materials [181, 192]. The JKR model is validated by experimental methods, incorporating a glass convex lens onto a polymer particle with a considerable reduction of the bulk modulus, which is heated above \(T_g\) following the effect of short-range surface forces [193].

The JKR model is unique in its ability to predict the force required to separate the particle from the surface, and the separation at a finite contact radius. If the applied removal force is considered to be a negative force, the JKR model predicts the Pull-Off force, \(P'\) that is required to detach the particle from the surface with which it contacts [184, 185]:

\[
P'_{\text{JKR}} = -\frac{3}{2}W_A\pi R
\]

(2-13)

In this case, \(a\) will decrease as \(P\) increases, where \(a\) must be positive in Eq.2-8 for it to permit a real number. The surfaces separate abruptly with a finite contact radius. The theory of JKR predicts that the separation initiates at a finite contact radius, \(a\) is given by \(a = 0.63a_0\).
In 1975, DMT [183] predicted that the Hertzian indentor has merit over the theory of JKR. The interaction of the particles are equally partitioned, with half coming from within the contact-zone and the other half outside, as illustrated in Figure 2.29.

![Figure 2.29 Schematic illustration of DMT short and long range forces at the contact zone.](image)

DMT predicted that the resulting contact radii was approximately half those found employing the JKR model. The DMT model calculates the contact radii based on molecular interaction. The contact radius for the DMT model is given by:

$$a^3 = \frac{R}{K} P + 2w_a \pi R $$  \hspace{1cm} (2-14)

Manipulating for the applied load, $P$:

$$P = \frac{4Ea^3}{3R} - 2\pi RW_a$$  \hspace{1cm} (2-15)

and the displacement, $\delta$ is given by:

$$\delta_{DMT} = \frac{a^2}{R} $$  \hspace{1cm} (2-16)

if no load is applied, then $a_0$ reduces to:

$$a_0^{3(DMT)} = \frac{2\pi w_a R^2}{K}$$  \hspace{1cm} (2-17)

Unlike the theory of JKR model, the theory of DMT predicts that the contact radius decreases with an increase of the applied load. Complete separation initiates when the contact radius equals zero. The Pull-Off force, $P'_{DMT}$ and equilibrium contact radius, $a_0$ predicted by the DMT model is given by:

$$P'_{DMT} = 2\pi W_A R$$  \hspace{1cm} (2-18)

And:

$$a_0^{(DMT)} = \frac{1}{1.82}a_0$$  \hspace{1cm} (2-19)
The JKR and DMT models predicted a 2/3 power-law, dependent on the contact radii of the particle radius under a zero load, and both models assumed only elastic deformation and a small contact radii. Considering the assumptions by Hertz, the contact radii that is predicted by the DMT model is half of that predicted by JKR model. A theory validating both JKR and DMT models in different cases was proposed by Muller, Yushchenko, and Derjaguin (MYD) [186]. This theory determined that the JKR model is increasingly suitable to contacts of large particles, high surface energy, and materials of high rigidity. The DMT model has enhanced suitability to contacts with particles of reduced size, low surface energy and materials of reduced rigidity [181]. A validity parameter has been established to distinguish between the JKR and DMT models employing a dimensionless parameter $\mu$ given by [187, 188]:

$$\mu = \frac{R^*(wa)}{E^{*2}Z_0^3} \quad (2-20)$$

$Z_0$ is the separation distance between the particle and substrate, assuming it is comparable to the interatomic separation distance of the solids bonded by van der Waals forces, it is assumed to be approximately 0.4 nm [191], and where $E^*$ is:

$$E^* = \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2}^{-1} \quad (2-21)$$

$E_1$ and $E_2$ are the Elastic Modulus of the substrate and particle. $R^*$ is the equivalent radius of the spheres and is defined as:

$$R^* = \frac{1}{R_1} + \frac{1}{R_2}^{-1} \quad (2-22)$$

Tabor predicted that the JKR model was valid for $\mu > 3$ and the DMT model is valid for $\mu < 1$ [187]. This is contradicted by MYD theory, which states the JKR model is valid for $\mu > 1$, and the DMT model is valid for $\mu < 1$. The theory of MYD has further been proven, where $\mu = 1$ was found to be continuous, displaying the transition between theories of JKR and DMT [194].

The JKR model has been successfully applied for the analysis of plastic deformation of metal micro-contacts by Maugis and Pollack (MP), referred to as the MP model [181]. The contact radius predicted by the MP is given by:

$$a^2 = \frac{P + 2\pi a R}{3\pi Y} \quad (2-23)$$
Where, $Y$ is the yield point of the material. If no load is applied, then Eq.2-23 reduces to:

$$a = \frac{2w_0}{3Y} \frac{1}{R^{1/2}}$$  \hspace{1cm} (2-24)

When plastic deformation is initiated, the theory of MP predicts a power-law dependence of the contact radius on the particle radius as $0.5$ [181]. The theory of MP has been proven for a contact radius of aluminium particles on a silicon substrate [188]. The adhesion induced contact radius of dry particles of PS and PU are sprinkled onto substrates and characterisation is achieved from imaging by field emission scanning electron microscopy (FESEM). The work of adhesion predicted by JKR and DMT models is large and unrealistic when comparing with theoretical values. Assuming plastic deformations ensues, the MP model predicts increasingly realistic outcomes which correlate with previous work [191]. The JKR and DMT models are based on small strains, while it is apparent that the effects of large stresses and strains appear to produce experimental outcomes that are not predicted by either theories of DMT or JKR. Particles in the sub-micrometre scale can have large adhesion properties, which results in plastic deformation and total engulfment of the particle in the substrate. Engulfment of a particle initiates at some radius, $R_{Eng}$ where the interfacial energy, $\gamma_{12}$ is sufficient to eliminate the particle. Engulfment of a particle during elastic deformation initiates when:

$$R_{Eng} = 7(\gamma_{12}/E)$$  \hspace{1cm} (2-25)

and for plastic deformation:

$$R_{Eng} = \frac{2\gamma_{12}}{3Y}$$  \hspace{1cm} (2-26)
The result is a $3/4$ power-law dependence over the theories of JKR and DMT values of $2/3$. An example of particle engulfment, where the contact radius is almost equal to the particle radius is presented in Figure 2.30.

![Figure 2.30 Nominal glass particles on a plasticised PS substrate, of radius (a) 4 µm, and (b) 11 µm][191].

The theories used in this study predict a smooth contacting surface, assuming a spherical NP, as presented by the scenario in Figure 2.31(a). When the roughness gradual increases, the contact with colloidal particles is not affected, as the due to the small sizes involved, as illustrated in Figure 2.31(b). The surface roughness of micro-scale proportions can lead to double contact by the lodging of NPs in voids where the theories of JKR and DMT are increasingly difficult to apply, as illustrated in Figure 2.31(c) [195, 196]. Here the force required to embed a NP, is no longer acting perpendicular to the contact surface. In the case of a rough surface, the NPs may contact the textile surface in multiple areas.

![Figure 2.31 Surface roughness types associated with adhesion of NPs. An ideally smooth surface (a), increasing roughness of surface (b), and a comparable roughness with the NPs dimension (c).]
2.5. Conclusions

Technical textiles in a health and hygiene environment are defined by physical properties, and are therefore an essential component in the future development of microbial inhibitors. The accumulation and adhesion of microorganisms on textile surfaces reduces the barrier efficacy to liquid strikethrough in textiles for the prevention of microbial growth.

The deliberate synthesis and control of NPs, which are particles of the nanoscale size that have extraordinary properties is considered a form of nanotechnology. As particle sizes reduce, the SA/V increases, where they provide enhanced chemical reactivity. The ability of particular NPs to degrade microbes by photocatalysis is a property that has captured the enthusiasm of the technical textile sector. Nanotechnology is now a key component in the research and development of self-cleaning, antimicrobial textile materials. TiO$_2$ for example, are photocatalytic NPs that have economic viability, chemical stability, and high efficiency as a photocatalyst to merit industrial application. The high cost of Ag, lack of chemical stability, and the difficulty in processing has restricted its employment as NPs for the incorporation into textiles for antimicrobial purposes.

Frequency of wavelength, barriers to illumination, light intensity, distance to surface, and type of NPs are factors that determine the required energy of light illumination for reactions with NPs incorporated on a textile surface. Containment, control and detection of airborne NPs are difficult. Incorporation of NPs into a textile fiber structure has reduced microbial activity, where a large presence of agglomeration exists.

The high working temperatures and ease at which they recover, distinguish thermoplastic polymer textiles as an ideal material for surface and structure manipulation. The viscoelastic region between, $T_g$ and, $T_m$ for thermoplastics can be manipulated by precise control of both thermal and loading conditions. The adherence of NPs to the exposed surface of a textile has presented the most efficient method of utilising light illumination.
Dip-coating, spin-coating and pad-dry-cure are popular methods of coating a polymeric surface with NPs. Sonochemistry is employed to deposit thin films by passing a material through an ultrasonic radiation machine. Sol-gel technology has been applied to a polymeric surface for increased adherences of NPs. Binders have also been employed to reduce sintering temperatures of polymers, assisting the adherence of NPs to surfaces. Electrohydrodynamic spraying produces small self-dispersing droplets on surfaces, with minimal adhesion presented between NPs and polymer surfaces. Electrospinning is the process of placing a polymer solution into a capillary and spinning it through a nozzle connected to multiple kilovolts of electrical fields. Surface treatments by RF, MW plasma and UV-irradiation are successfully employed to activate and enhance the adherence of NPs to polymer surfaces. Each of these techniques has their own strengths and limitations when considering the coating of the frontal surface of a textile product to render self-cleaning properties into the textile.

The bonding mechanism between NPs and textile surfaces are a critical factor to examine the durability of the incorporation and functional life. An adhering system between two substrates is a result of either chemical or physical bonding by interfacial forces of attraction, achieved through the interactions of atoms, ions and molecules. Adhesion in the system can be measured experimentally by work of detachment or separation between the two surfaces. Contamination of either adhering surface through surface defects or soilage permits an effect on the adhesion in the system. The Hertzian indentor was the first theory designed to consider the adhesion forces acting between two rigid contacting bodies. JKR, DMT and MYD are all theoretical models designed to quantify the Pull-Off force of two-rigid bodies. No conclusive evidence exists, to present the suitability of the JKR, DMT or MYD models as the best suited to quantify the Pull-Off force required to detach a solid or elastic particle from a solid or elastic substrate.
3. Methodology and Experimental Techniques

This chapter detailed the materials, design principles, experimental rigs, analytical techniques, and methods of durability testing employed in this study. The novel procedure for embedding of NPs into thermoplastic textile surfaces, and a description of the efficient use of the SA/V of NPs was detailed and supported with relevant illustrations. There was a description of the design and construction of the manual, semi-automatic and automatic embedding rigs, and details of the NPs and textiles initiated with the novel processing technique. A description of the advantages and limitations of analytical techniques including DSC, DMA, SEM, EDX and AAS was provided. Test methods, standards and equipment employed to quantify the adhesion of NPs to textile surfaces were discussed. Durability testing in the form of a domestic laundering standard was discussed as a technique of evaluating the adherence of NPs to textiles.

3.1. Materials

This section introduces the materials employed in this study. A description of the textiles used as the host material for embedding of NPs was described with the mechanical and thermal properties sourced from literature. Characterisation of textiles was provided by imaging using SEM, showing the weave pattern of the PET fibres and the porosity of the textiles. A description of the NPs used, and the concentration of solution for analytical techniques by AAS was also provided.

3.1.1. Textile Substrates

Commercially available thermoplastic polymer textiles were selected for embedding of NPs to surfaces and comparative assessment during temperature and the optimisation of the concentration of NPs. All textiles were woven fabrics, and were of different mass, porosity, and weave pattern. The textile samples, if not specified, were employed as received from a local retailer. The main characteristics of textiles employed were listed in Table 3.1.
Table 3.1 Characteristics of textile host material for embedding of NPs by hot-pressing. [1, 11, 12, 14, 15]

<table>
<thead>
<tr>
<th>Textile</th>
<th>Colour</th>
<th>Weave</th>
<th>Density (g/cm³)</th>
<th>Break Strength (MPa)</th>
<th>Melting Temp. (°C)</th>
<th>Glass Transition Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>White</td>
<td>Warp &amp; Weft</td>
<td>1.39</td>
<td>48 - 72</td>
<td>260</td>
<td>80</td>
</tr>
<tr>
<td>Acrylic</td>
<td>Brown</td>
<td>Warp &amp; Weft</td>
<td>1.19</td>
<td>69</td>
<td>170 - 190</td>
<td>115</td>
</tr>
<tr>
<td>CA</td>
<td>Pink</td>
<td>Warp &amp; Weft</td>
<td>1.22</td>
<td>13 - 62</td>
<td>250</td>
<td>-</td>
</tr>
</tbody>
</table>

Imaging by SEM of PET, acrylic and CA textiles used in this study were presented in Figure 3.1. PET textiles had a highly porous structure of 45%. Acrylic and CA textiles both had low porosity of 5% and 10% respectively.

Figure 3.1 SEM images of thermoplastic polymer textiles used in this study, PET (a), acrylic (b) and CA (c).

3.1.2. Nanoparticles for Incorporation

The NPs chosen for this study was TiO₂, which was the most common photocatalyst available. The properties of TiO₂-NPs have been discussed in Section 2.2.2. Commercially available forms of inorganic TiO₂ were employed in this study. The source and basic properties of the TiO₂ were as specified by the supplier and presented in Table 3.2. The fractions of TiO₂ employed were 80/20, anatase to rutile respectively. The TiO₂ was received in a 1 litre container and dispersed in a surfactant. The concentration of TiO₂ in the surfactant was 40 wt.%. The TiO₂-NPs were of spherical shape, and an average diameter of 50 ± 3 nm that was measured by SEM imaging.
Table 3.2 Descriptive of ENM source for adherence of NPs to textile surfaces.

<table>
<thead>
<tr>
<th>ENM</th>
<th>Description</th>
<th>Manufacturer</th>
<th>Average Particle Size (nm)</th>
<th>Concentration of TiO$_2$ in surfactant (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Degussa Aerosil W741X (Evonic®)</td>
<td>Lawrence Ind. Ltd</td>
<td>50</td>
<td>40</td>
</tr>
</tbody>
</table>

All other solvents, materials, chemicals and reagents employed in this study were of the analytical grade. Distilled water was employed for preparation of concentrations of TiO$_2$ in the treatment of the textile. Hydrofluoric Acid (HF) 48% AR supplied by Scientific & Chemical Supplies Ltd. was employed for the formulation of AAS studies.

3.2. The Textilise™ Process

In the following sections a discussion of the techniques applied to embed NPs into a textile surface by manual, semi-automatic and automatic embedding rigs was detailed. A description of the design principles and the equipment employed to prepare textiles with NPs embedded on surfaces was outlined, with the aid of schematics and drawings throughout. Supplementary drawings and models of embedding rigs designed by computer-aided design (CAD) techniques were provided in ‘Appendix B’.

3.2.1. Design Principles

The incorporation of NPs into the surface of a polymer was an important step in the development of a textile material embedded with NPs permitting photocatalytic properties. Embedding into surfaces should not involve total engulfment of the NPs [191], but the NPs should retain a presence to the outer surface of the textile fibers for photon exposure. The major difficulty with surface incorporation of microbiocidal agents into textiles lies in the durability of adhesion and binding of these agents to the surface of the textiles.
Textile fibres are made of either natural or synthetic polymers or a blend of these two. It is usually the frontal surface of a textile product that is exposed to the ambient environment, and therefore contact with surface for microbial contamination. This surface was therefore considered more prone to the growth and spread of microbes, also discussed in Section 2.1. This frontal surface also has the greatest exposure to photons from sunlight or any suitable artificial light source that can more effectively cleanse the textile surface through photocatalytic actions, for example. The microbiocidal actions take place at the surfaces of these metal based microbiocidal agents, which means that a higher amount of surface area exposed to the ambient will result in a larger extent of surface reactions to degrade microbes.

Textiles coated with NPs on both sides of the surface, are mostly modified by methods incorporating chemical preparation techniques, like sol-gels [135, 146, 197], or surface preparation techniques including UV, RF and MW plasma treatments [140, 148, 149, 198]. As discussed in Section 2.3, chemical and surface preparation techniques amplify the bonding of a coating to a textile surface. A continuous coating of microbiocidal agents on textiles is not required due to the colloidal nature and finite size of microbes during the planktonic stage of growth, during which the microbiocidal action is most effective. A continuous coating also has the limitation of resulting in a weaker interface due to the inherent difficulty in achieving a strong bonding with a surface of a textile over a large surface area. A thick coating emphasises this problem by further weakening the interface due to the difference of elastic properties between the harder metal-based microbiocidal agents and the soft and compliant matrix of the textile. This increases the risk of dislodgement of NPs during use as clothing products and when exposed to cleaning procedures. It also significantly reduces the SA/V of the NPs that would have been otherwise available to kill bacteria.

The procedure of embedding NPs described in this section provided a safe, durable, environmentally safe, inexpensive and industrially scalable technique for producing antimicrobial polymeric textiles using microbiocidal NPs. The textiles embedded with NPs in the present study have been distributed as a fine dispersion on single-side of the textile surface, without the formation of a surface coating of NPs. This significantly reduced the quantity of NPs required for efficient killing of
microbes. The process permitted efficient employment of the SA/V properties of a NP. A strong bonding was achieved by utilizing the thermoplastic nature of the polymeric by modifying the surface of the textile without adversely affecting the bulk properties, such as appearance or colour. The NPs were distributed over the textile surface as individual particles or as small agglomerates, as described by the schematic illustration in Figure 3.2(a). The procedure resulted with a single-sided, non-continuous distribution with separated NPs which do not form any thick film or coating on the surface, and as such reduced the risk of flaking, peeling or delamination of coatings that can arise from a continuous or thicker coating.

In the instance where NPs have been dislodged from the fiber surface, any peel or rupture that would generally initiate on a surface coating cannot exist with individually dispersed NPs. The exposure of the fiber surface was minimised to that individual nanoparticle area, as the neighbouring NPs permitted protection of the exposed area by the close proximity that exists through their efficient dispersion, as described in Figure 3.2(b).

![Figure 3.2 A plan view schematic illustration of Distribution of NPs (a), and efficient SA/V ratio for effective activity (b).](image)

The textile surface layer was modified by thermal treatment, where the textile was heated above the thermal transition, $T_g$, but below, $T_m$, to a depth less than or equal to the diameter of the NPs to be embedded within its surface. The deposition of NPs by dispersion was initiated prior to thermal treatment of the textile surface. The one or more NPs were deposited in a manner such that they were distributed as small agglomerates or as individual NPs where possible, across the surface of a single-side
of the textile surface, where no formation of a film or continuous layer was permitted. A sufficient quantity of heat was then applied to the textile surface after distribution of NPs, to soften the surface for displacement (δ) by embedding of less than or equal to the diameter of the NPs, as described by the schematic illustration in Figure 3.3. Pressure by way of a clamp was applied to the NPs on the textile surface, which facilitated the embedding process. Heat was applied to modify the surface of the textile. When the textile cools, it recovered from its softened state and provided a stronger bonding due to mechanical interlocking of the embedded NPs within the fiber surface. On conclusion, the design principles can be summarised as:

1. Single-sided coating of textiles by NPs
2. Dispersed rather than a uniform coating of NPs on the surface
3. Optimised embedding of NPs to maximise the surface area exposure to light for photo excitation.
4. Optimised embedding to improve the adherence and durability of NPs to textile surfaces.
5. Minimise damage to the textile integrity.

![Figure 3.3 A schematic illustration displaying a cross sectional view of a textile fiber with NPs embedded. 1-5 relates to scenarios of NPs embedded into frontal surface. Scenario 1: High light exposure, low durability of NP; Scenario 5: Low light exposure, high durability.](image-url)
Figure 3.3 provided a schematic illustration showing different extents of embedding of spherical NPs into a cooled thermoplastic textile surface that was previously softened by the application of heat:

I. point contact adhesion with the weakest bonding to the textile surface results with a maximum exposed surface area of NPs for photon exposure

II. partial embedding with slightly stronger bonding with the textile surface but also with a slightly reduced surface area for photon exposure than in case I

III. optimal embedding with strong bonding with the textile surface although with smaller but still sufficient surface area for photon exposure

IV. sub-optimal embedding with increased bonding with the textile surface but with a significantly reduced surface area for photon exposure than in case I to III

V. Engulfment of NP, permitting the strongest bonding with the textile surface but with no surface area for photon exposure.

In the case of a spherical NP, the penetration depth by displacement, $\delta$ was defined by the diameter of the spherical NP, i.e $0 \leq D \leq \delta$. Exposing the maximum surface area for antimicrobial action, and the maximum penetration for stronger bonding initiated when $\delta$ approached half the diameter of the NP ($D/2$), was considered as the desired combination for optimal durability of NPs to surfaces while presenting sufficient photon exposure of the NP surface. In the case of non-spherical NPs with a long dimension, $D$ and short dimension, $d$ the best combination of surface area and bonding was obtained when $\delta$ approached half the shortest dimension ($d/2$).

3.2.2. Manual Hot-Pressing of Textiles

NPs were applied to textile surfaces by a 3.2 ml. polyethylene transfer pipette. Hot-pressing of textiles was achieved employing a Toni & Guy™ Tournaline hair straightening iron, as presented in Figure 3.4. The hot-iron had two ceramic plates for clamping, where both plates were in the range of the same temperature, ±3 °C. The temperature was manually set by the operator, using a dial on the hot-iron
handle. When the hot-iron ceramic plates were clamped together, the temperature of the ceramic plates fluctuated by ±6 °C. This created a difficulty when optimising the embedding process for efficient activation temperatures of the textile surface. The dual side heating also permitted embedding of both sides of the textile surface, which was an undesirable feature of a coating of NPs as discussed in Section 3.2.1.

Figure 3.4 Manual embedding apparatus: Toni & Guy™ Tournaline hot-iron.

The hot-iron was modified by applying a heat-shield of 80 gramme of paper to one of the heated ceramic plates, termed the “non-embedding” side. The hot-iron was modified for hot-pressing of single-side of a textile, with the temperature of the non-embedding side reduced to 85°C. The hot-iron temperature was manually adjusted by a temperature setting on the hot-iron handle. A thermocouple was employed to assess the temperature of the heat resistant and embedding sides of the device. The maximum temperature of the hot-iron was recorded as 197°C. Upon deposition of NP solution by pipette to the textile surface, the textile was placed on the non-embedding side of the hot-iron. Embedding of NPs was finalised by reducing the embedding side of the hot-iron onto the textile surface, and the manual application of a clamping force was applied.

This technique presented textile surfaces with single-side embedded with NPs. The NPs were finely dispersed, but there was an inhomogeneous distribution of NPs over the textile surface, especially between replicate samples. The limitations of this technique included the manual clamping of the hot-iron, the inefficient clamping
temperature, and the small size of the hot-iron, and were factors that affected the homogeneity of sample replicates.

3.2.3. Semi-Automatic Embedding Technique

The control and automation of the hot-plate temperature and the distribution of finely dispersed solution of NPs was a factor in the scale-up of the process to the semi-automatic embedding rig. The automatic control of the hot-plate temperature permitted the optimisation of the textile embedding temperature. A finely distributed application of NPs permitted the dispersion of NPs as individual or small agglomerates over the textile surface. Preparation of textiles in an isolated environment permitted the protection for the operator from atomised NPs. The automatic clamping of the hot-iron was another factor that enhanced quality of process optimisation, and the homogeneity of replicate samples.

A Sealey™ Shot Blast cabinet (Spray box) (0.6 x 0.5 x 0.5 m³) was employed as a protection box, where it enclosed both the spray and hot-pressing step during the processing of textiles. The shot blast cabinet was fitted with an air vacuum extractor system. A modified Breville™ VST012 Sandwich Press or hot-press (HP) was installed in the box. The HP floating top-surface was employed as the hot-pressing device. A voltage of 110 VDC was supplied to the HP to heat its top surface. A Eurotherm™ 91e PID controller was employed to control the surface temperature of the HP surface. A thermocouple was positioned on the reverse side of the HP surface. The thermocouple output was input to the PID controller. The maximum stable temperature of the HP was 169°C. The voltage to the HP was switched employing a 3A relay which was controlled by the PID controller.
Figure 3.5 Shot blast box with PID temperature controller and air vacuum extraction system (a), hot-press and spray-gun housed in the protection box (b).

A Draper Tools™ spray-gun was used to supply a finely dispersed solution of NPs at a flow rate of 0.045 ml/sec to the textile surface. Nitrogen gas was used to bring the solution through the nozzle of the spray-gun, and a pressure regulator was fitted to control the pressure. The spray-gun had an atomised spray pattern, as presented in Figure 3.6. In the processing of spraying the textile samples with NP solution, the operator of the spray-gun had to wave the spray over the textile surface for the distribution of NPs over the entire textile surface area.

Figure 3.6 Spray pattern from a Draper Tools™ spray-gun.
A solution reservoir of 20 ml was fitted to the spray-gun. The textile sample was placed on a stainless steel holding plate (0.1 x 0.12 m²), and retained in position by securing the edge of the textile to the plate’s underside with two-sided adhesive-tape. Spraying of the textile was manually operated and applied from a vertical position. After spraying, the embedding side of the HP surface was immediately closed on the textile. An embedding force was applied to the HP by its own weight, which was equivalent to 9 N. The force \((F)\) applied to the HP was quantified by employing the mass, \(m\) of the weights, and the gravitational constant, \(g\).

\[
F = mg
\] (3-1)

Upon application of the embedding side of the HP surface, an initial reduction in temperature was noted, which was monitored and accounted for in the analysis. This reduction was, on average between 3°C to 5°C, and returned to the set-point after 10 seconds. The vacuum system was opened after the HP had been removed from the textile surface. The textiles were retained in these conditions for 5 minutes. After this extraction period, the protection box was opened, and the textile samples were removed.

The semi-automatic embedding rig permitted greater consistency of replicate samples compared to that of the manual technique. Textiles were successfully embedded with NPs on single-side of its surface; i.e. the side that was sprayed with NPs and then in contact with the HP surface. The spraying of NPs initiated a fine dispersion over the textile surface. This technique permitted the quantification of concentration (wt.%) range for the applied concentration of NPs to the textile. However, the manual operation of spraying permitted a wavy effect of NPs over the entire textile sample. This waving effect of NP spray was clearly visible during microbiology testing. As the maximum stable temperature of the HP surface was 169°C, this was considerably lower than the melting temperature of most common thermoplastic textiles, such as: PET, acrylic and CA, for critical temperatures of the textiles see Section 3.1.
3.2.4. *Automatic Embedding Technique*

Accommodation and integration of a NP embedding process into an existing textile facility was an essential factor in the design of a facility for an automatic embedding rig. Minimising the manual interaction and bottlenecks was an essential task in the production of an embedding process of NPs suitable to industrial facilities. This was achieved by creating continuous movement of a textile through a hot-pressing system. The key factors that were considered in the design and fabrication of an automatic embedding rig were;

- Textile transfer rate through the process
- Flow rate of solution onto the textile
- Nozzle-spray delivery type
- Concentration of NPs delivered to the textile surface
- Temperature of embedding surface
- Force applied to the textile during hot-pressing
- Thermal conductivity of the non-embedding side

A schematic illustration of the automatic embedding rig layout was presented in Figure 3.7.

![Figure 3.7 Schematic illustration of the automatic embedding rig, plan and processes. 1: Transfer roller; 2: Cleaning blower; 3: NP spray-nozzle; 4: Hot-plate and calendar roller pinch point; 5: Retrieved textile; 6: Retrieval of excess NP solution.](image-url)
1. The textile pay-off was positioned on a transfer-roller (TR), where the textile was transferred through the embedding process. The textile transferred over a combination of 31.75 mm diameter TR, made of 304 SS tube 0.28 m in length. The TR was centred on M6 threaded bar and pivoted on Zn caps (40 x 40 mm²) from MBS™, as displayed in Figure 3.7.

2. A cleaning blower (CB) was used to remove dust and loose fibers present on the textile surface. Compressed air at a pressure of 100 kPa was applied over the textile. The compressed air was controlled by a solenoid valve, which permitted air flow through an 80° Arag Group™ flat fan nozzle.

3. The spraying solution was stored in a 5 litre polypropylene container. A 24 VAC Aquatec™ CDP 8800 Pressure boost pump delivered the solution through 3/8” Nyflex™ polyurethane tubing. The tubing was transferred to a BJ0023 73 Even Fan nozzle supplied by BeteUK™. This nozzle sprayed solution onto the textile surface through an angle of 73°, at 0.048 l/min, and a pressure of 1.5 bar, and was displayed in Figure 3.8.

4. The textile was transferred and pinched between a HP and calender roller (CR). The HP was made from 5 mm, 304 stainless steel plate. A 450W/230V mat-heater was glued to the HP by Dow Corning™ 736 hi-temperature glue, and was displayed in Figure 3.8. An M6 K-Type ring-washer thermocouple was positioned on the underside of the HP and connected to an Omron E5CK digital controller. The HP retained a homogeneous thermal stability over its surface, and a maximum temperature output of 232°C, which was verified by an external thermocouple and display unit. Two springs with a stiffness of 80 N/m were positioned on the HP, and maintain the pinch between the HP and CR. The CR was fabricated from a 41 mm diameter billet of Stavax 1.2083. The CR rotates on 12 mm ID FS 4 bolt bearing units positioned at its ends. A Vexta™ 5 Phase 0.72” stepper motor which was connected to the CR, and drove the textile between the CR and HP, as displayed in Figure 3.7.
5. The embedded textile was retrieved on a TR. The TR pivots on 12 mm ID bearings located at its ends. A Vexta™ 5 phase 0.72” stepper motor drove the TR by pulling the textile through the pinch between the HP and CR.

6. A PET container was situated under the embedding rig for the retrieval of excess solution.

Figure 3.8 Images of spray delivery nozzle (a), the hot-plate assembly (b), and cotton calender roller (c), from the automatic embedding rig.
A combination of Profile 8 (40 x 40 mm$^2$) and Dexion™ Angle 140/s was employed to construct the rig frame. The frame dimensions were 1.33x0.6x1.16 m$^3$. The frame was covered with 5 mm thick clear Lexan™ polycarbonate sheeting and insulated with Stormguard™ door and window seal, positioned around the edges of the frame and doors. An access panel was positioned at both ends of the rig frame and on its upper side. All access panels were hinged using stainless steel butt hinges. Locking of the panels was achieved through stainless steel bolting devices. The rig was an insulated unit, with motors, controls, display and drivers located outside the rig, as displayed in Figure 3.9.

Figure 3.9 Motors, control, display and drivers of automatic embedding rig (a & b).
A schematic layout of the operating systems and controllers for the automatic embedding rig was presented in Figure 3.10. Two National Instrument (NI) DAQ Pad-6015 devices provided the required Input/Output (I/O) signals that operated the automatic embedding rig. The DAQ Pad devices provided plug-and-play connectivity via USB, for acquiring, generating and logging data. Direct connectivity of the DAQ Pad was achieved through screw terminals for signals and sensors. The Labview™ software permitted communication with the DAQ Pad device through a user interface on a PC. The Labview™ programme was employed to control:

- Velocity of the stepper motors in m/s
- On/off delivery of solution to the nozzle
- Compressed air to the cleaning blower.

![Figure 3.10 Control layout of fully-automatic embedding rig prototype.](image)

Compressed air was supplied through a 24 VDC Airtac™ single acting solenoid valve, until the CB control was switched by Labview™ on the control monitor. When the CB control was switched, a 5 volt signal was sent from a NI DaqPad-6015. The NI Daq pad subsequently sent 5 volts to a Super Vexta™ 5 phase processor, which sent a signal that opened the switch and permitted the 24 VDC supply voltage to be grounded, thus opening the solenoid valve and allowing compressed air to be released through the CB nozzle. The Aquatec™ CDP 8800
Pressure boost pump was supplied with 24 VDC converted to 24 VAC by a transformer. When the relevant control in Labview™ was switched, current was delivered to the pump which supplied solution to the nozzle at a pressure of 500 kPa and a flow rate between 1.9 to 2.6 LPM. The pressure and flow rate of the spray was dependent on the nozzle fitted to the rig.

The TR and CR were powered by Vexta™ 5 phase 0.72” stepper motors. The motors were connected to the rollers by aluminium clamp couplings. Labview™ controlled the velocity of the stepper motors, by providing an appropriate number of pulses to the motor controllers. An Omron E5CK digital controller was powered by 230 VDC mains supply. The controller supplied 230 VDC to two 450W/230V mat heaters.

3.3. Analytical Techniques
This section details the characterisation and analytical techniques used to characterise the NPs and textile surfaces. A description of the equipment used including DSC, DMA, SEM, EDX and AAS was provided, with critical procedures and limitations detailed.

3.3.1. Microstructural Analysis by SEM
A sample surface is displayed by an SEM by scanning the surface with a high-energy beam of electrons in a raster scan pattern. Signals are created by the electrons interacting with the atoms on the sample, which contain unique information about the samples composition, topography and electrical conductivity [199]. Radiation signals produced by the SEM include secondary electron emission, X-ray emission, back scattered electrons (BSE), light (cathode luminescence), specimen current and transmitted electrons [200]. With the addition of specialised detectors to the SEM, these signals can be gathered from the sample and translated into various types of material information such as chemical composition, surface topography, electrical conductivity and crystallography.
The most common detection mode on the SEM is the use of secondary electron imagining (SEI). Secondary electrons are used for imaging of both rough and polished surfaces. Low energy and positive potential of the detector makes collection of electrons highly efficient. On this detector there is a high resolution option, rendering it possible to view surfaces in the region of 1 to 5 nm in size, depending on the material under analysis [201]. Images are generated by electron beams produced by heating of a tungsten filament cathode inside the electric gun, as detailed by the schematic illustration in Figure 3.11. Tungsten’s high melting point, low vapour pressure and low cost are reasons for its use in thermionic electron guns [75, 200]. With the lowest vapour pressure of all metals, this permits heating for electron emission. The first beam passes through a condenser lens and focused as a spot approximately 0.4 nm to 5 nm in diameter on the sample surface using an objective lens.

![Figure 3.11 A schematic of scanning electron microscope (SEM) operating system.](image)


Reproduced from [75]
Imaging can be used to control or enhance contrast, reduce noise and identify features as the screen picture is generated from an electrical signal. Advantages related to SEM imaging include [75, 199, 200];

- Improved resolution and magnification than that of optical microscopes.
- Increased spatial resolution.
- A larger depth of field.
- Energy saving.
- Easily operated, and a large space available for dynamic experiments.

A Hitachi™ SU-70 SEM with a field emission electron source fitted with a tungsten filament was employed for the microstructural analysis of the textile samples. Samples were prepared for characterisation by SEM by placement of a layer of 12 mm Agar Scientific™ carbon two-sided adhesive tape to the sample stub, then placement of the textile on the carbon tab [13]. It was recommended that an operating SEM voltage of 5 kV be employed for analysing polymer surfaces [75], but this low voltage reduced the resolution of the image. It was highlighted that this voltage was mostly a requirement for analysing fractured polymer surfaces, which was not the focus of the present study. When analysing polymers it was recommended to work with and test differing voltages to gain an understanding of the particular sample. An operating voltage of 10 kV was employed for textile samples in this research.

Most samples are electrically non-conductive, giving them an electrical resistance when imaging by SEM. Coating a sample with a conductive layer of carbon or metal like gold (Au), for characterisation by SEM was a method employed to prevent the build-up of electrons. The coating was deposited on the sample surface by vacuum deposition [75]. A uniform covering of the conductive material was applied to the textile surface. The coating was applied in a glass chamber, and the coating was distributed through a needle valve that was provided with low pressure argon gas. A thin coating permitted minimal traces of charging during imaging by SEM, while a thick coating presented an efficient conductor, but may have hidden important details of the sample surface and therefore negatively affect microanalysis [91, 200]. Within this research, Au was employed to coat the samples for imaging and analysis by EDS. An Emitech™ K550 sputtering machine was employed to coat
samples with Au. Upon optimisation of sputtering of samples, a current of 30 mA was employed for this study, with varying sputtering times dependent on the type of analysis required. Mapping by EDS techniques required a 2 minute deposition of Au, while imaging by SEM required 1.5 minutes of Au deposition.

3.3.2. Microstructural Analysis by EDS

The Energy Dispersive Spectrometer (EDS) is an attachment to the SEM technique. It is a vital detector that offers rapid evaluation (10-100s) of qualitative and quantitative analysis of sample constituent’s [200]. An X-ray analyser detected the elements that were present on the textile sample, and the location and concentration of NPs.

The EDS was firstly employed to confirm the presence of NPs on the textile surface. Secondly the EDS technique was employed to map a selected surface area of the textile sample. Mapping of the surface permitted the quantification of percentage coverage of NPs on a particular element of the selected mapping area. Mapping of selected elements was achieved, where the primary materials under investigation been TiO$_2$ and PET textiles, the main elemental components investigated were Oxygen and Carbon from PET, and Ti from TiO$_2$-NPs.

It was possible for two x-rays to arrive at the detector in the exact same instance of time, where they were considered as a single x-ray. These x-rays appeared as an extra peak at twice the correct energy. A disadvantage of the EDS detector was its vulnerability to high temperatures, therefore requiring the detector to be cooled by liquid nitrogen. Limitations of the EDS included [75, 199];

- Spectral interference at voltages < 3 keV, which included elements below Carbon on the periodic table.
- Limited detection capabilities for elements below sodium on the periodic table.

The EDS is a variation of X-ray fluorescence spectroscopy, which is based on an assessment of the selected sample through interactions among electromagnetic radiation and matter, by measuring the energy and intensity of distribution of the x-
X-ray mapping is a popular method of analysing elemental information due to its specificity and high-quality visual presentation. X-ray information can be displayed as spectra, line scans or x-ray maps [200]. Spectra images were employed during this study. They are produced by feeding the x-ray information from a given element back into the SEM. Mapping is achieved by the detection of an x-ray photon, with the EDS set to selected energy windows around peaks. This initiates the photographic cathode ray tube (CRT) system to record a red dot at the position of the scanned beam and a grouping of red dots is placed against a the image background [199, 200]. The image background represents the absence of that element. In this study, selected regions of the sample were taken and analysed for percentage of Ti present in that region of the sample.

The EDS detector provided rapid evaluation of qualitative and quantitative analysis of sample constituent’s [200]. An Oxford Instruments™ X-Max Silicon Drift Detector 50 mm² was attached to the SEM. The detector in use was a lithium-silicon (Si(Li)) diode. The EDS was employed for two characterisation purposes in the current research:

1) Confirmation of the presence of NPs on the textile surface by Point ID analysis.

2) Mapping and quantification of NPs on a selected surface area of the textile surface.
3.3.3. *Atomic Absorption Spectroscopy (AAS)*

Atomic absorption spectroscopy (AAS) is a popular analysis technique employed for analysis of metal and metalloids. It is a highly sensitive process that analyses absorption of radiant energy by atoms. The addition of heat permits a change of the energy state of an atom to an excited state, and it is this change of energy ($\Delta E$) relative to an atom stable or ground state that is measured, as illustrated by the schematic in Figure 3.12.

![Figure 3.12 Principles of the atomic absorption spectroscopy process (AAS).](image)

Heat permits an increase of the total atom population, while also increasing the thermal emission and absorption signals. Atoms increase the energy state in levels known as transitions. Where sufficient energy is input and absorbed in an atom, there is an increase from the ground state, $E_o$ to the first excited state, $E_1$ which is equal to $\Delta E$. The energy can be initiated into these atoms by way of UV light, where atoms of different elements use specific wavelengths. AAS techniques uses the relationship between energy transition and wavelength to quantify the presence of specific elements, dependent on the absorption of the elements at particular wavelengths [202]. The relationship between each energy transition and wavelength, $\lambda$, where, $h$ is the Plank’s constant, is described by the equation:

$$\Delta E = \frac{h}{\lambda}$$  \hspace{1cm} (3-2)

Analysis of NPs by AAS techniques was either in a solid or liquid phase, where the NPs must undergo desolation or vaporisation into a gaseous state by a flame or graphite furnace. The resulting analyte ions or atoms permitted absorption of UV or visible light, and initiated the transition to an increased energy state, where the analyte concentration was assessed by the quantity of absorption. Solutions were aspirated with the gas flow into a nebulising or mixing chamber to form small droplets before entering the flame, as illustrated in Figure 3.13.
Figure 3.13 Schematic illustration of an atomic absorption spectrometer (AAS). Adapted from [203]

Four replicates (4 x 4 cm²) of each embedded textile sample were analysed. Samples were placed in 100 ml a high density polyethylene (HDPE) flask. 10 ml of HF was added to the sample, which was then sealed and manually agitated for 10 seconds by hand before storing in a fume hood for 18 hours. 20 ml of distilled H₂O was added to the HDPE flask and the solution was thoroughly mixed before quantification by AAS. Textiles were analysed using a Spectra AA 200 fitted with a hallow cathode lamp containing a Ti element with a wavelength of 364.3 nm, employing a modified version of ASTM 4563-02 [204]. AATi1-5 produced from Inorganic Ventures™ was employed as a Ti standard to calibrate the AA spectrometer, where a calibration curve was formulated pre analysis of the embedded textiles. Concentrations of textiles containing TiO₂-NPs were correlated with the working curve of the calibration measurements. A conversion parameter was applied to convert AAS output of mg/l of Ti to µg/cm² of TiO₂. This conversion parameter was provided in ‘Appendix D’.

3.3.4. Differential Scanning Calorimetry (DSC)
Differential scanning calorimetry (DSC) measures the thermal effects of a material by comparing its weight change while it is exposed to controlled rates of temperature in a furnace under a gas atmosphere, such as air, nitrogen or a vacuum [205]. A material of known mass is heated and cooled to desired temperatures, where the heat flow of the material is measured as changes in heat capacity.
The basic principles of testing a material by DSC include the assessment of different thermal transitions including latent heat, or changes in heat capacity of that material [205, 206]. Limitations of the DSC technique using TA Instruments equipment include: the difficulty with assigning a baseline; and the availability of quality standards. The advantages of DSC lie with the ability to produce data at a fast rate, and the efficiency of data.

In this study, a baseline was first measured by using a standard reference material that exhibited no transitional change to temperature; here two empty pans were used. The sample materials were then situated inside individual samples and reference holders, as illustrated in Figure 3.14. Aluminium pans were used in this study, which are the more common type of holders used in this technique. Effective and reliable data was achieved by permitting good thermal contact between the material, pan and heat flux plate. A gas flow through the pans provided the sufficient atmosphere, assisting the heat transfer and restricting contamination from volatile elements [206]. Heating of the pans was provided by an electric current supply to each holder by way of a heat flux plate. A thermocouple monitored the temperature of each holder, and supplied this information to a CPU. The CPU permitted control of the furnace, retrieved the data signal, and enabled analysis of the data. The data was plotted by comparing the difference in energy that was supplied to the material against the average temperature [205].

Figure 3.14 Schematic illustration of a TA Instruments™ DSC. Adapted from [205, 206]
DSC experiments were applied using a Perkin Elmer Pyris 1 calorimeter connected to an intercooler. Two empty aluminium pans were used to set the baseline, when the DSC was run to a temperature of 300°C. These reactions were achieved at a cooling/heating rate of 10°C/min in the temperature range of 30°C to 300°C, where helium was employed as the purge gas. Samples were cut from textiles and tested as received. Sample sizes were approximately 0.1 mg each, and placed in 50 µl aluminium pans (0.1 x 2.1 mm²) supplied by Perkin Elmer™, ensuring that the samples made good contact with the pan and cover. The DSC instrument was calibrated for energy with two empty 50 µl aluminium pans.

3.3.5. Dynamic Mechanical Analysis (DMA)

The DMA exhibits a sinusoidal deformation by applying a controlled stress or strain onto a material of a known geometry. The DMA was an enclosed unit, free of any external temperature effects. The textile sample was placed between two clamps situated at vertical ends of the textile, as illustrated in Figure 3.15. The fixed clamp held one end of the textile statically, while the second clamp had freedom to oscillate. The oscillating clamp was connected to a force motor by a drive shaft, where deformation of the sample was generated [207]. The temperature of the enclosed unit was measured by a thermocouple situated under the oscillating clamp. A linear voltage differential transformer (LVDT) recorded the position of the oscillating clamp, where the information was relayed to a CPU. The material deformation was directly related to its stiffness. The limitations of the technique relate to the differences between DMA and data from other common thermal transition instruments such as analytical techniques by DSC and thermomechanical analysis (TMA). The differences were considered acceptable, so long as the outcomes were related to those standards that they were tested [207].
The mechanical properties of textiles were assessed by using dynamic mechanical analysis (DMA). The testing was initiated according to standard methods of ASTM D4065-06 [208]. An ATA DMA Q-800 instrument was employed in this study. A film/fiber tension clamping kit, supplied by Waters Chromatography™, was fitted to the DMA for the analysis of textiles at elevated temperatures. PET films (41 x 6.3 x 0.09 mm³) were employed as calibration specimens. The DMA was set to a ramp rate of 5°C/min, a maximum strain and temperature of 0.5% and 210°C respectively. The dimensions of PET textile were measured and input in units of millimetres, and a value of poisson’s ratio of 0.4 was recorded from literature. The temperatures applied to dynamic testing was below the melting temperature, as melting of the textiles would initiate damage of the instrument.

3.3.6. Design of Experiments (DOE) and Sources of Error
All outcomes were the arithmetic mean of specimens analysed from each sample, and their respective standard deviations were presented in Chapters 4 to 6. The means of treated samples were compared with the respective controls employing the Wilcoxon related t-test, and it was assessed if they were statistically different for a confidence level of 95% [209]. IBM™ SPSS Statistics 19 and Minitab™ 16 statistical software were employed for quantification of data. Regression lines were
examined by calculating the total sum of squares (TSS), and the regression sum of squares (RSS) of residuals [210].

3.4. Nanoparticle Adherence to Textile Substrates

3.4.1. Pull-Off Strength

A PosiTest™ AT-A was employed with a modified version of ASTM D4541-09 in this study [211]. The PosiTest™ AT-A operated by use of an electronically controlled hydraulic pump. It was a standardised tool for the measurement of coating adhesion, such as paint and render to surfaces like metal and concrete. An interchangeable dollie, which acted as a force applicator, permitted analysis of varying areas of textile surfaces. The dollie employed in this experiment was of 20 mm diameter. Pull-rate speeds ranged from 0.2 MPa/sec to 125 MPa/sec and were varied by 0.1 MPa/sec increments. A textile sample (0.12 x 0.1 mm²) was clamped to a stainless steel holding plate by PP two-sided tape, with the embedded side of the textile facing upward, as illustrated in Figure 3.16.

![Figure 3.16 Posi-test AT-A head unit, dolly and NP embedded surface. Adapted from [212]](image-url)
The 20 mm dollie was initially coated with PP two-sided adhesive tape. To optimise the Pull-Off test, it was determined that the two-sided adhesive tape was difficult to remove, and became distorted after a test. Consequently, a layer of single-sided adhesive tape was applied on top of the two-sided adhesive tape, with the adhesive side facing outward. The result was an easier removal of the adhesive-tape and enhanced preservation of the test specimen after running a test. The stand-off on the Posi-Test™ AT-A was positioned over the dollie and held in a perpendicular position to the sample plane, as illustrated in Figure 3.17.

![Figure 3.17 Schematic illustration of Pull-Off test specimens.](image)

The Pull-Off test was initiated until destruction, where the single-sided PP adhesive-tape pulled away from the textile surface. The Pull-Off result was recorded and displayed in units of stress (MPa). The PosiTest™ AT-A permitted Pull-Off of a PP adhesive-tape from a NP embedded textile surface. This was applied until the adhesive-tape fractured from the textile surface. The tensile force required to Pull-Off a coating from a surface area can be employed as a pass/fail analysis of the test. The resultant adhesive-tape sample was characterised by EDS and AAS analytical techniques. Due to the very low surface concentration of NPs on the embedded textile specimen, 12 repetitions of the Pull-Off test was achieved, where separate 12 dollies were performed, as presented in Figure 3.18(a).
As HF is non-corrosive to most thermoplastic polymers, the dollies were designed and fabricated from HDPE at the University of Limerick. The 12 dollies were situated for AAS studies in a purpose built rig fabricated from PE material, and then positioned in a PE container, as displayed in Figure 3.18(b). Dissolution of the entire dollie surface area was achieved by suspending the dollie above the base of the PE container.

3.4.2. Laundering of Textiles
A Whirlpool™ 850 AWG 384 domestic washing machine was employed in accordance with the standard ISO 6330:2008, for laundering of textiles. The 1.5 kg mass in the drum was achieved by adding two pillows, 0.75 kg each, to the wash chamber during cycles of laundering. A common domestic washing detergent, Fairy™ Non-Bio laundering detergent was employed in this study as the reference domestic washing detergent during cycles of laundering. Inputs of the Whirlpool™ 850 AWG 384 for this study were presented in Table 3.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>Run Time (min.)</td>
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</tr>
<tr>
<td>Spin Speed (revs/min)</td>
<td>700</td>
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<tr>
<td>Temperature (°C)</td>
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<tr>
<td>Quantity of Detergent (mg)</td>
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</tr>
</tbody>
</table>
3.5. Conclusions of Experimental Techniques

The steps taken to design a novel method of embedding textile surfaces with NPs was discussed in this chapter. On the foundation of this model, the design principles, materials, experimental techniques, characterisation methods and durability testing was outlined. The materials used in this study were selected based on the ease of availability to consumers and the applicability to textiles used in the medical environment.

The design principles highlighted a novel method of incorporating NPs by using physical methods to embed them into textile surfaces that have been thermally softened by the addition of heat [10]. A thermoplastic polymeric textile was deemed the best material for this type of process. Utilising the thermoplastic polymers softened state when at temperatures above glass transition temperature, $T_g$ [1, 2], this method anchors the NPs by physical interactions [147, 213], with the textile surface. Finely distributed and dispersed NPs on the textile considerably increase the active interfacial surface area [214, 215].

Distribution of NPs in a controlled formation was applied by optimising the concentration of the selected solution. The process provided an adaptable technique of activating polymer based thermoplastic textiles, through a simple, fast, efficient, low-cost and adaptable process. The textile prepared in this research, becomes an effective and reusable antimicrobial textile that retains its microbiocidal activity after cycles of laundering.

This experimental study employed commercially available AERODISP® W 740 X containing 40 wt.% of TiO$_2$ (Evonic®) in a form of water suspension purchased from DegussaTM, with an average particle size of 50 nm. The fractions of TiO$_2$ employed were 80/20, anatase to rutile respectively. Distilled water was employed for preparation of concentrations of TiO$_2$ in the treatment of the textile.
The main thermoplastic textile employed during this study was a commercially available 100% PET textile, with 45% porosity. The popularity of PET textiles in the medical industry has been widely known, incorporating products such as gowns, drapes and curtains. The thermal properties of this textile correlated with values from literature. Commercially available CA and acrylic textiles were the other textiles employed to verify the experimental process.

A manual rig was employed for the embedding of NPs to textile surfaces. On application of a concentration of TiO₂, a modified and manually operated hot-iron clamp was used to apply heat to single-side of a textile surface for surface softening and physical embedding of NPs by clamping. The experimental methods incorporated an up-scaling of the initial rig, where this was dependent on the optimisation of the previous rig.

When the outcomes of the embedding technique by manual rigs was achieved, a semi-automatic rig was constructed based on these outcomes. Application of TiO₂ by a manual spray was initiated for finely distributed NPs, and a controlled temperature of the hot-plate clamping. Outcomes of the semi-automatic rig highlighted the importance of spray atomisation.

An automatic embedding rig was constructed with the continuous transfer of the textile under a fixed spray-nozzle and clamping by a hot-plate and calender roller. The automatic rig successfully produced a continuous textile with efficient and optimised distribution of NPs on its surface.

The textiles coated with TiO₂ were characterised for shape, size, distribution of the NPs, where these properties of the sample textiles were examined using a Hitachi SU-70 SEM equipped with an Oxford ISIS 300 EDS micro-analytical system. Content of TiO₂ on textiles was quantified by techniques of AAS, using a Spectra AA 200, with a Ti element of 364.3 nm in wavelength. The techniques and equipment employed to achieve characterisation of textiles were considered state of the art in the field of analytical instruments that they operate.
Dynamic and static thermal transition in thermoplastic textiles was achieved by DSC using a Perkin Elmer Pyris 1 calorimeter connected to an intercooler. This technique permitted assessment of the glass transition temperature and melting temperature of textiles, which were important characteristics to this study. Dynamic thermal transitions were assessed by DMA using an instrument from ATA DMA Q-800. The temperatures applied to dynamic testing was below the melting temperature, as melting of the textiles would initiate damage of the instrument.

Durability of textiles embedded with NPs was successfully assessed by domestic laundering standards, [216], but direct Pull-Off forces employing a modified standard for the adhesion of coatings proved difficult to quantify.

Statistical analysis was an important technique used to evaluate the significance of experimental data and also design the empirical models. The means of treated samples were compared with the respective controls employing the Wilcoxon related t-test, using a confidence level of 95% [209]. IBM™ SPSS Statistics 19 and Minitab™ 16 statistical software were employed for quantification of data.
4. Embedding of Nanoparticles to Thermoplastic Textiles: Theoretical Considerations

This chapter presents the theoretical considerations of embedding of NPs into thermally softened thermoplastic textile surfaces. These considerations permitted an understanding of the static and dynamic thermal response of thermoplastic textiles under a strain. The thermal response of PET textiles was introduced, where DSC thermoanalytical data was provided. The dynamic thermal response of NPs under a normally applied load to a PET textile fiber was quantified and detailed by DMA techniques, as detailed in Section 3.3.5. The elastic modulus of the textiles was then incorporated into both the JKR and DMT theories of contact mechanics, as discussed in Section 2.4.2. This provided the quantification of contact radius, \( a \) displacement, \( \delta \) and force, \( P \) of a spherical embedded NP into a PET textile surface, as presented in Figure 4.8 to Figure 4.11, where a value for \( \text{Pull-Off force} \), \( P_{\text{Pull-Off}} \) was also provided. The theory assumed that the contact geometry was that of an indented rigid NP on a rigid compressible thermoplastic textile fiber with no surface roughness present.

4.1. Thermal Response of Textiles by DSC
PET, CA and Acrylic textiles were analysed for the static thermal transitions by DSC techniques. The thermal transitions by DSC were provided in Figure 4.2 to Figure 4.4. DSC techniques were employed to measure the heat flow (mW/g) and the temperature (°C) of a material, where the associated transitions of that material were then presented. Such transitions were used to qualify the chemical and physical changes in a material, which involved the exothermic and endothermic processes [156]. An ideal DSC analysis of a thermoplastic PET material was presented in Figure 4.1.
The melting temperature, $T_m$ and glass transition temperature, $T_g$ of the PET textile were successfully assessed by DSC techniques. The DSC profile of a PET textile were compared to transitions in common thermoplastic materials, and of PET profiles that were studied in the literature [1, 9]. The peak at 70°C indicated an endothermic reaction, where heat was required to flow into the PET for it to maintain its temperature, as highlighted in Figure 4.2. This was the temperature where $T_g$ initiated, where the amorphous chains required thermal energy that initiated their vibration and loosening. As the temperature increased, the amorphous chains can form and align themselves in an ordered crystal lattice. At 150°C a cold crystallisation, $T_c$ exothermic reaction of PET was present. Continuous heating above the crystallisation temperature permitted a second endothermic reaction to initiate at 235°C. This indicated the presence of $T_m$, and related to the melting of the crystalline region [9].
The thermal response of CA textiles was presented in Figure 4.3. The $T_g$ of CA textiles was difficult to examine, where the endothermic peak was assumed to initiate at approximately 60°C. The second endothermic reaction initiated at 245°C, where the $T_m$ of the textile was present. The $T_m$ of CA textiles was marginally lower than that reported in the literature, where a value of 250°C was recorded.

![Figure 4.3 Thermal response of CA textiles by DSC analytical techniques.](image)

The DSC profile of acrylic textiles correlated with common thermoplastic materials, and of acrylic profiles studied in the literature [9, 12]. The thermal responses of acrylic textiles were presented in Figure 4.4. Acrylic textiles had a short $T_g$ region, where an endothermic reaction was initiated at 70°C. The textile had a delayed transition of $T_m$, compared to the value in literature, as presented in Table 2.1, which was recorded between 170 to 190°C. As highlighted, the endothermic transition correlating to $T_m$ was present at approximately 265°C. There was a continuous endothermic reaction present throughout the thermal heating of the material, which indicated a linear reduction of the textiles mechanical properties with increasing temperature.
Figure 4.4 Thermal response of Acrylic textiles by DSC analytical techniques.

The thermal activation temperature, $T_a$ of thermoplastic textiles was applied for a normalised parameter $\tau$. Employing $T_g$ and $T_m$ of the textile, at an active temperature, $T_a$, the processing temperature for embedding techniques can be normalised for $\tau$, where:

$$\tau = \alpha / \beta$$

(4-1)

Here, $\alpha$ can vary with $T_a$:

$$\alpha = T_a - T_g$$

(4-2)

And $\beta$ is fixed by, $T_m$ and, $T_g$ for a given thermoplastic textile material:

$$\beta = T_m - T_g$$

(4-3)

4.1.1. Summary

When no load was applied to a PET textile, the analysis by DSC predicted a $T_g$ phase change at 70°C, thereby enabling a stiff to rubbery state of the material. The phase change from rubbery to a viscoelastic state initiated where $T_m$ was 235°C, approximately. The phase changes were assessed by approximating the distinctive peaks of heat flow activated by the thermal change. The phase changes for CA thermoplastic textiles initiated at 60°C and 245°C for, $T_g$ and, $T_m$ respectively. The phase changes for acrylic thermoplastic textiles initiated at 70°C and 265°C for, $T_g$ and, $T_m$ respectively.
4.2. Thermal Response of PET Textiles Under a Dynamic Load

The dynamic response of thermoplastic textiles was achieved by incorporating techniques of DMA as discussed in Section 3.4.5. The dynamic responses by DMA were employed to study effects of temperature on the elastic modulus of PET textiles under a strain. Secondary transitions such as, \( T_g \) in thermoplastic polymers, can be quantified by oscillating the material in a temperature ramp [217]. Since segmental transitions were associated with a maximum in energy dissipation, in this study a peak in the elastic modulus (MPa) was employed as an indicator of the elastic modulus relaxation.

4.2.1. Thermal Response of PET Thermoplastic Polymers by DMA Techniques

Figure 4.5 presented an idealised response of thermoplastic materials achieved by DMA techniques [218, 219]. The \( T_g \) was represented by the peak on the storage modulus axis \( E' \). \( E' \) was the energy stored elastically during deformation of the material, and was related to the elastic modulus of solids. A steady rate of modulus declined between temperatures of -25°C and 25°C. Chains within crystallised regions of the structure vibrated, where the applied strain permitted the chains to slide over each other, and allowing the increase of elasticity and plasticity of the structure. The material then translated to a rubbery state between temperatures 25°C and 75°C. The applied strain initiated early stage plastic deformation, where elongation of the material existed. Here the material fully plastically deformed, i.e. went beyond its elastic limit, where the applied strain cannot be recovered. The loss modulus \( E'' \), represents the energy converted to heat during deformation. Loss tangent, \( \delta \) represents the phase lag between the applied stress and the measured strain.
The DMA was calibrated with a PET film supplied by Waters Chromatography™. The thermal response of the elastic modulus of a PET film was presented in Figure 4.6. The thermoplastic response of a PET film followed a similar profile to that recorded in literature [1]. The elastic modulus of the PET film was established as 3,200 MPa when strained to 11% in ambient conditions. The elastic modulus declined at a steady rate by 70% between 70°C and 120°C. The transition to $T_g$ at 80°C was recognised by the intersection highlighted. The PET film then went into a rubbery state between 120 and 230°C, where the modulus was between 900 and 500 MPa. Here the crystalline regions of PET were reduced. At this time the PET film went into a viscoelastic region, where the amorphous regions were viscous like. The PET was not recoverable at this point, and plastically deformed when increasing strains were applied, going beyond its elastic limit and eventually breaking [9].
The outcomes identifying the thermoplastic response of a PET textile when 6 N of load was applied were presented in Figure 4.7. The textile had an elastic modulus of 390 MPa when a load was applied in ambient conditions. The elastic modulus of the PET textile reduced at a slower rate than that of the calibration film presented in Figure 4.6. This was considered a factor of the high thermal conductivity of the textile, where the porous fibrous material distributed heat and strain over several fibers and permitted a reduced relaxation of the modulus. A 35% decline in elastic modulus between 80 and 110°C was observed. The PET then went into a rubbery state, where increasing molecular motion created by temperature and the applied strain initiated the breaking of secondary bonding between chains. This was present in the amorphous region or soft region of the PET, where chains were now permitted to slide over each other due to the applied strain. It is known that crystalline chains are difficult to breakdown, as they are neatly branched and organised, as presented by the schematic illustration in Figure 4.7 [45]. At this point the textile was beyond the thermal transition of $T_g$, and increasing the temperature between 110 and 193°C severely reduced the modulus from between 250 to 139 MPa. Here the crystalline region of PET was experiencing an increasing chain vibration. This region was termed the viscoelastic region, where a partial flow of the
PET structure was noted [1]. Above 193°C, the applied strain was sufficient to plastically deform the PET and take it beyond its elastic limit. The final modulus was recorded at 139 MPa, where $T_a$ was 193°C.

![Diagram showing the relationship between the elastic modulus and temperature of PET textiles when a constant strain was applied.](image)

Figure 4.7 The relationship between the elastic modulus and temperature of PET textiles when a constant strain was applied.

4.2.2. Summary

The modification of elastic modulus was achieved for a PET textile by applying dynamic thermal responses, where its reaction to dynamic loading depended on the composition, crystal structure, and orientation of the textile material [45]. Heat treatment had little effect on the elastic modulus, so long as it did not affect the aforementioned parameters. At increasing temperature, a reduction of the elastic modulus was expected due to thermal expansion and increasing amplitude of atomic vibrations. The thermal effects of the mechanical properties have increasing effects on polymer films. Enhanced plasticity typically contributed an increase of the surface to surface adhesion, as more energy was dissipated through the plastic deformation than through the crack growth [221].
The thermal response of PET textiles under an input load was assessed by techniques incorporating a DMA instrument. This presented effects of the applied strain on the elastic modulus of PET, CA and acrylic textiles. The thermal response of PET at 40°C initiated an elastic modulus of 390 MPa, while at 193°C the elastic modulus was 139 MPa. This highlighted softening of the PET at elevated temperatures, which related to outcomes by DSC methods in Section 4.1. Elastic response of PET textiles followed a similar profile to the PET calibration film, where the material was a hard and stiff surface until $T_g$ was reached, and then softened to a rubbery state in the viscoelastic region just before melting of the material initiated at $T_m$.

4.3. Mechanism of Contact between the NP and PET Textile Surface
The adhesion mechanism of a spherical NP of TiO$_2$ on a PET fiber surface was based on theories incorporating contact mechanics. Properties of TiO$_2$-NPs and PET textiles described in Section 3.1 were utilised in theories of JKR and DMT, as listed in Table 2.11. The characterisation of physical and mechanical properties of TiO$_2$-NPs require complex computational modelling, to avoid this, relevant properties of the elastic modulus at 40 and 193°C, the surface energy, $\gamma$ and the Poissons ratio, $\nu$ have been reviewed from the literature [222]. Previous work indicated that a reduction of the Poissons ratio size had a minimal effect on the fundamentals of the theories. A value of 0.45 for Poissons ratio was employed for the TiO$_2$-NPs and, 0.4 for PET textiles, as based on literature [182, 223-225]. TiO$_2$-NPs have large surface energies, $\gamma$ where a value of 2 J/m$^2$ has been reported [226, 227]. PET textiles have a lower surface energy, $\gamma$ where a value of 0.04 J/m$^2$ has been reported [228]. Employing Eq.2-9, the combined work of adhesion, $W_a$ was calculated to be 0.57 J/m$^2$. Surface characterisation by imaging using SEM techniques was employed to quantify the diameter of TiO$_2$-NPs detailed in Section 3.1.2, where an average diameter of 50 ± 5 nm was recorded. The elastic modulus, $E$ of PET textiles at 40 and 193°C was examined using analytical techniques by DMA, as discussed in Section 4.2.
Table 4.1 Properties of TiO₂ NPs and PET textile materials for theoretical analysis.

<table>
<thead>
<tr>
<th>Material</th>
<th>TiO₂</th>
<th>TiO₂ Source</th>
<th>PET</th>
<th>PET Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic Modulus, $E @ 40^\circ C$ (MPa)</td>
<td>22,000</td>
<td>[229]</td>
<td>390</td>
<td>DMA</td>
</tr>
<tr>
<td>Elastic Modulus, $E @ 193^\circ C$ (MPa)</td>
<td>22,000</td>
<td>[229]</td>
<td>139</td>
<td>DMA</td>
</tr>
<tr>
<td>Surface Energy, $\gamma$ (J/m²)</td>
<td>2</td>
<td>[222, 226, 227]</td>
<td>0.04</td>
<td>[1, 228]</td>
</tr>
<tr>
<td>Radius, $R$ (nm)</td>
<td>25</td>
<td>SEM Imaging</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Poissons Ratio, $\nu$</td>
<td>0.45</td>
<td>[222]</td>
<td>0.4</td>
<td>[1, 225]</td>
</tr>
</tbody>
</table>

The effect of surface temperature was investigated on the contact radius, $a$ and the displacement, $\delta$ between a spherical TiO₂-NP and PET fiber surface, with the outcomes presented in Figure 4.8 and Figure 4.9. The PET surface was optimised for contact with a NP where the temperature dependent elastic modulus, $E$ was examined by DMA techniques, as presented in Figure 4.7. The elastic modulus of a PET textile was considered temperature dependent, while the surface energy and poissos ratio of PET was considered constant at elevated temperatures. The elastic modulus and the radius of curvature of a TiO₂-NP were considered to be unaffected by temperature changes. A modulus of 390 MPa for PET textiles at 40°C was quantified from the data presented in Figure 4.7. At this temperature, the properties of the contacting surfaces best resemble the materials properties when at ambient conditions. The elastic modulus of PET at 193°C was taken to be 139 MPa.

4.3.1. Contact Radius of TiO₂-NPs on Fibers of PET

Figure 4.8 and Figure 4.9 present the contact radius and displacement of a NP in a PET fiber using both JKR and DMT models, where the PET textile was at 40 and 193°C. A schematic illustration of the contact profile between the NP and fiber surface was also provided. The short-range adhesion of a NP using the JKR model permitted a contact radius of 10 nm, where no displacement into the fiber surface was initiated. The large contact radius was a factor of the adhesion forces that acted at the contact area. As the contact radius increased, the NP displaced into the fiber surface. On full contact of the NP, a displacement into the fiber surface of 18 nm was
recorded. The contact of spherical NPs with the surface of a PET fiber was achieved using the JKR model, and permitted deformation of the contact geometry, as described by the schematic illustration in Figure 4.8(a). [193]. JKR also considered the molecular attraction between the NP and fiber surface, which increased the contact area and displacement [190]. Contact between surfaces using the DMT model predicted an adhesionless contact model, where the forces of molecular attraction that acted across the gap of the NP and fiber surfaces had no effect on the displacement or contact radius of the NP [189]. There exists no contact radius of the NP when no contact deformation existed, as described by the schematic illustration in Figure 4.8(b).

![Figure 4.8](image_url)

**Figure 4.8** The theoretical contact radius and displacement of a TiO$_2$ NP on a PET fiber surface at a temperature of 40°C and an elastic modulus of 390 MPa. Schematic illustration of JKR contact (a), and DMT contact surface (b), for TiO$_2$ NP adhesion to PET textile fibers.

The change in elastic modulus of PET textiles had an effect on the displacement of NPs into the fiber surface when values were initiated with theories of JKR, as presented in Figure 4.9. The contact radius increased to 15 nm from 10 nm, when at reduced modulus and displacement of the NP in the surface. At this
contact radius, dislodgment of a NP from a PET fiber surface was initiated. The outcomes from the DMT model were unchanged from those presented in Figure 4.8, as the elastic modulus of the materials had no effect on the contact adhesion between surfaces of materials, these outcomes are similar to those found in literature [191].

![Theoretical contact radius and displacement of a TiO$_2$ NP on a PET fiber surface at a temperature of 193°C and an elastic modulus of 139 MPa. Schematic illustration of JKR contact (a), and DMT contact surface (b), for TiO$_2$ NP adhesion to PET textile fibers.](image)

**Figure 4.9** The theoretical contact radius and displacement of a TiO$_2$ NP on a PET fiber surface at a temperature of 193°C and an elastic modulus of 139 MPa. Schematic illustration of JKR contact (a), and DMT contact surface (b), for TiO$_2$ NP adhesion to PET textile fibers.

### 4.3.2. Effect of the Applied Load on the Contact Radius of TiO$_2$-NPs to PET Textile Fiber Surfaces

The force required to adhere a NP of TiO$_2$ onto a PET fiber surface was achieved, where a contact radius between the NP and fiber surface was initiated at textile temperatures of 40°C and 193°C. The elastic modulus of PET textile at 40 and 193°C was examined by dynamic testing using DMA techniques, where 390 and 139 MPa were initiated for the temperatures, respectively. The force recorded using the theory of DMT at a contact radius of 25 nm was greater than that predicted by the theory of JKR, 313 nN and 75 nN respectively. Adhesion forces of JKR were inactive until a compressive force initiated the contact between the NP and PET surface, where the short-range tensile forces acted only inside the contact area and radius of the NP, as described by the schematic illustration in Figure 4.10(a) [181, 193]. In the JKR
model, contact deformation of the contact area was initiated by the short-range attraction between the NP and the fiber surface. The adhesion forces increase with an increase of the contact radius, identified by the presence of a large negative load. The load-displacement achieved by the JKR model agreed with previous work in this area, where large adhesion forces were present between particles in contact with solid surfaces [193, 223, 230]. The minimum value of load predicted by the JKR model was 66 nN, and represents the Pull-Off force required to detach the NP from the fiber surface when no load was applied, as highlighted in Figure 4.10. This value for Pull-Off force correlates with the value calculated by the JKR model, using Eq. 2-13.

The DMT model presented an external adhesive force or long range forces where minimal contact of the NP to the PET surface existed. These forces acted outside the radius of contact of NPs with PET fiber surfaces, and acted as an additional force [224]. The normal stresses were compressive at the contact area, while adhesive stresses were tensile at the edge of the contact area [182, 190]. The adhesion force calculated was 88 nN, as highlighted in Figure 4.10. The geometry of the contact by DMT model was restrained, where deformation of the fiber surface was present when in contact with a NP, as described by the schematic illustration in Figure 4.10(b). The Pull-Off force by DMT model was achieved using Eq.2-18 (2RW_{a}r), and quantified a value of, 88 nN. The Pull-Off force related to the adhesion that existed between the NP and the fiber surface, and also the force required to detach the NP from the fiber surface. The DMT force had an asymptotic increase with increasing contact radius of the NP. The Pull-Off force quantified using the DMT model was greater than the Pull-Off force predicted using the JKR model. This comparison related with previous work in the area of micrometre sized polymer particles on glass and silicone substrates [224].
Figure 4.10 Theoretical contact radius of a TiO$_2$ NP on a PET fiber surface with an elastic modulus of 390 MPa. Schematic illustration of JKR contact (a), and DMT contact surface (b) for NP adhesion to PET surface.
Figure 4.11 presented a theoretical examination of the displacement of a NP into a PET fiber surface at a temperature of 193°C, where the elastic modulus of the PET textile was 139 MPa. The theory of JKR predicted a larger contact radius for a reduction of adhesion force, as presented in Figure 4.11. The data indicated that a reduced elastic modulus of the PET had permitted an increasingly compliant surface for embedding of NPs. The Pull-Off force of a NP was calculated as 66 nN, which was similar to the Pull-Off force recorded when the PET textiles were initialised at a temperature of 40°C. The Pull-Off force was related to the work of adhesion between the NP and the fiber surface, and the radius of the NP, but was considered independent from the elastic modulus of the contacting surfaces [184]. As the contact was considered adhesive, the theory of JKR related the contact to the elastic properties and the interfacial interaction strength [224]. When no load was applied, there existed adhesion forces between the contact areas where the NP and fiber surface was in contact. A contact radius between the NP and fiber surface remained before detachment of the NP was initiated, as described by the schematic illustration in Figure 4.11(a).

In the theory of DMT, the contact radius increased with increasing compressive forces. Like the JKR model, the DMT model also permitted an increasingly compliant fiber surface when at a higher temperature. The embedding force was reduced to 60 nN for a contact radius of 25 nm at the elevated temperature of 190°C. The NP initiated using the DMT model was fully dislodged from the PET fiber surface when no displacement of the surface was observed. The NP was still adhered to the PET surface by long range adhesion forces. This permitted the prediction of a Pull-Off force of 89 nN, where the elastic modulus of PET had no effect, as described by the schematic illustration in Figure 4.11(b).
Figure 4.11 Theoretical contact radius of a NP of TiO$_2$ on a PET fiber surface with an elastic modulus of 139 MPa. Schematic illustration of JKR Pull-Off surface (a), and DMT Pull-Off surface (b) for NP adhesion to PET surface.

4.3.3. **Summary**

As a method of assessing the adhesion mechanism of NPs to PET fiber surfaces, a theoretical approach incorporating models of JKR and DMT from contact mechanics theory were initialised. The models proved beneficial for assessing the adhesive response of NPs to thermally modified thermoplastic surfaces. The models of JKR and DMT were applied to a NP of TiO$_2$ that was in contact with a PET fiber surface. The elastic modulus of PET textiles while under an applied load of 6 N, and at temperatures of 40 and 193°C were initialised with the JKR and DMT models. The
theory of JKR allowed for a non-zero contact radius at zero displacement and zero loads. Due to the adhesive contact achieved, this adhesion was initiated during the unloading cycle, and also passed into the negative loading zone. The elastic modulus of PET fabrics had no effect on the contact radius initiated using the DMT model. This outcome indicated that no extra displacement was to be gained from thermally altering the PET fiber surface.

The adhesion that existed for NPs embedded in a PET fiber surface was higher for the DMT model than that predicted by the JKR model. The JKR model was more sensitive to the elastic modulus of the PET surface than the DMT model. This was due to enhanced sensitivity of the adhesive forces when the stiffness and the size of the contacting materials were reduced [223]. The contribution of surface energy affected the linearity between the applied load and the real area of contact. At a reduced load, the area of contact experienced negative contacting loads due to the surface energy [224]. An increasing adhesion energy initiated increased displacement of NP depth into the fiber surface, where the DMT model had increasing sensitivity to the adhesion energy compared [224]. As adhesion energy increased, differences between the displacement depth assessed for the JKR and DMT models also increased. The theory of DMT was noted as fully elastic, where molecular interactions like Van der Waals forces were permitted. These interactions were considered to be outside the contact radius, which initiated a rise to an additional load.

The two variant theories of contact mechanics discussed in this chapter have provided an understanding of the contact area between NPs embedded in thermoplastic textiles experience. Theories of both JKR and DMT have indicated that increasing the softening of surfaces by thermal modification permits increased embedding of NPs into those surfaces for lower loads. The adhesion forces required to adhere a NP to the surface of a PET fiber can be substantially reduced by increasing the surface temperature of the textile towards the fibers $T_m$. Reduction lower elastic modulus also permitted an increase of the contact radius for a reduction of the applied load.
The Pull-Off force required to remove a NP from a PET fiber surface permitted a direct quantification of the surface energy measurement between the contact materials. As the elastic properties of the materials were not considered a factor of the Pull-Off forces measurement, adhesion energy was a function of the surface energies of the contacting materials, and the size of the NP. Outcomes from the models of JKR and DMT show that both the contact radius and the displacement of the NP had no effect on the adhesion energy between the NP and PET contact. Here the thermal alteration and subsequent surface-softening of the PET fiber had no effect on the energy required to detach a NP from its surface. Surface-softening did permit a reduction of the force required to embed a NP into the PET fiber surface.

4.4. Conclusions
Thermoplastic textiles heated above the glass transition temperature, \( T_g \) allowed for an increased compliance of the textile surface for embedding of a NP under an applied load. The semi-crystalline structure of thermoplastic materials permitted a temperature increase up to the melting temperature, \( T_m \) with no plastic deformation of the material. The crystalline chains retained formation at temperatures below, \( T_m \) where they permit recovery of the material [1, 9]. The heating of thermoplastic textiles and subsequent loosening of crystalline chains coincided with a reduction of the elastic modulus, and thereby initiated a reduction of the force required to embed NPs while an increasing contact radius and displacement was permitted into the fiber surface. NPs were embedded with a force that overcame the elastic limit of the thermoplastic textile fiber surface, and plastically deformed the fiber surface at the point that the NPs were in contact.

Dynamic mechanical testing of a thermally increasing thermoplastic polymer textile presented an effect on the elastic response by the application of an applied load. A thermal increase of the textile material permitted a reduction of the elastic modulus, where increasing plastic deformation of a PET textile was initiated at higher temperatures, from 240°C under no load, to 193°C when the load was 6 N. A maximum value for the normalised active temperature, \( \tau \) was 1, however as examined by analytical techniques using the DMA instrument, a load applied to a
thermoplastic textile where $\tau$ increases towards 1 initiated a premature plastic deformation of the textile. Therefore, a dynamic value of 0.7 for $\tau$ was achieved before plastic deformation of the fabric.

The mechanical and physical properties of PET thermoplastic textiles and TiO$_2$-NPs, sourced from literature and experimental techniques, were applied to theories of contact mechanics. JKR and DMT models were two variants of contact mechanics theories. Outcomes of the study highlight that embedding of NPs was better described by the JKR model [223], due to its higher sensitivity to the reduction of the textile stiffness, the size of the NP and the type of textile. The enhanced sensitivity to adhesive forces was associated with the reduction of the stiffness and size of the NP and textile. Reducing the elastic modulus of PET textiles permitted an increasing contact radius of the NP on its surface for a lower applied load.
5. Embedding of Nanoparticles to Thermoplastic Textiles: Experimental Results and Discussion

This chapter presents the outcomes of the application of the design principles discussed in Section 3.2.1 by experimental techniques, to incorporate NPs to thermoplastic textiles, and discussed the implications of various parameters in doing so. The study utilised characterisation techniques for the optimisation of the textile by methods discussed in Section 3.4. Adherence of NPs to textiles was examined by methods described in Section 3.4, where parameters such as the applied concentration of TiO$_2$, hot-press active temperature and clamping time of the hot-press parameters were optimised for processing.

The current chapter was organised by the methodological approach outlined in Section 1.4, presenting the experimental embedding of NPs to textile surfaces by employing the techniques discussed in Section 3.3. These techniques were:

2. Semi-automatic process of embedding of NPs to textile surfaces by application by spray-gun and hot-press.
3. Automatic process of embedding of NPs to textile surfaces by spray-nozzle and hot-press.

The effect of the applied concentration of NPs to the surfaces of textiles for embedding was detailed and discussed for the effect on surface distribution of NPs and adherence by durability testing. Outcomes of a Pull-Off test employed for quantifying the adherence of NPs to textile was presented and discussed. The quantitative measurements for assessment of the distribution of NPs on textiles by EDS mapping techniques was presented. Finally, the outcomes of durability testing presenting the retention of NPs to textiles was discussed. The outcomes enable the analysis of the effective hot-press active temperature, $T_a$ and the effective starting concentration to textile surfaces.
5.1. Manual Embedding of NPs to PET Textiles

NPs that were embedded to textiles surfaces by manual rigs have been discussed in Section 3.3.1. TiO$_2$ and PET, as described in Section 3.2, are the NPs and textiles respectively. The presence and quality of distribution of NPs on PET textiles was confirmed by SEM and EDS analytical techniques, as presented in Figure 5.1. A 0.15 wt.% concentration of TiO$_2$ was initiated by using a pippet to apply 5 ml. Of solution to the textile surface. The hot-press, with a 0.7 value for $\tau$, was clamped down on the textile, where $\tau$ is the normalised thermal active temperature of the hot-plate, and was discussed in Section 4.1.

Textiles showed a light discolouration of white to brown after hot-pressing. This was attributed to the charring and smoke fumes by the heat resistant paper, which discoloured the textile. A spectrum by EDS shows a clear presence of Ti on the textile fiber surface at the highlighted point, as presented in Figure 5.1(a), where no presence of Ti exists at the point highlighted in Figure 5.1(b). The surface characterisation by SEM displays good distribution of Ti in sporadic areas on the frontal surface of fibers, Figure 5.1(a). An inhomogeneous distribution of Ti exists over the fiber surface. On the underside of the fibers there was less distribution of NPs observed, compared to the top-side, as highlighted in Figure 5.1(b). This outcome could be an effect of a reduced heat present on the underside of the textile.

![Figure 5.1 SEM images of TiO$_2$ embedding to PET textile fibers by manual embedding techniques, and EDS spectrum analysis presenting a presence of Ti at the point of interest (a), and uncoated surface (b).](image-url)
It was further found that increasing the applied concentration of TiO₂ to 1 wt.% had no effect on the efficiency of distribution of NPs over the textile, as presented by Figure 5.2(a-c). TiO₂ was heavily agglomerated on the fibers, with inefficient distribution of NPs over the textile surface area, Figure 5.2(a). A large presence of TiO₂ droplets was evident where agglomeration of NPs at fiber boundaries was highlighted. Such large agglomerates produce an inhomogeneous film formation on the fiber surface. Under high-resolution, enhanced detail of NP contact to the fibers was observed, Figure 5.2(b). The NPs had increased distribution, where a clear presence of individually dispersed NPs on the fibers was displayed, as presented in Figure 5.2(c). Efficient distribution initiated an increasing SA/V of NPs applied to surfaces. The non-embedded side of the textile had large agglomerates at the fiber boundaries, as highlighted in Figure 5.2(d). This agglomerate film was due to the TiO₂ solution filtering through the fibers, onto the bottom surface of the hot-press. As the hot-press was partially insulated from heat on the non-embedding side of the hot-press, there still exists an opportunity for adherence of NPs to the non-embedding side by immersion coating [135, 136]. This coating resembles a surface film, as it was flaky at the fiber boundaries. The characterisation of images highlighted the need for control of the NP application to textiles.

![Figure 5.2 SEM images of PET textile prepared by manual embedding techniques, employing an applied concentration of 1 wt.%], presenting large agglomerates of TiO₂ (a), high-resolution imaging of dispersed NPs (b), areas of TiO₂ coated and uncoated PET fibers (c), and non-embedded side (underside) of PET after hot-pressing (d).
5.1.1. Summary

TiO$_2$-NPs were successfully adhered to thermally activated textiles by manual embedding rigs. A hot-press was employed to affect a clamping pressure at the NP to textile interface, and initiate increase of the textiles surface temperature. An increasing temperature of the textile surface, initiated chain vibration within the thermoplastic textile, where the elastic modulus was then reduced and the surface had an increasing compliance to the embedding of NPs. Low applied concentrations of TiO$_2$ (wt.%) presented enhanced efficiency of distribution of NPs on surfaces after clamping by hot-press, with optimum concentrations in the range of 1 to 0.15 wt.% of TiO$_2$. Large agglomeration and film formation of NPs on the embedding side of the textile were due to the increase of the applied concentration of TiO$_2$. The non-embedding side of the textile retained NPs on its surface, where the solution of TiO$_2$ had flowed through the fiber boundaries. This created a film formation on the non-embedding side of the textile, where the adherence of NPs and increased film formation was a consequence of immersion during hot-press clamping.

5.2. Semi-Automatic Embedding of PET Textiles with TiO$_2$-NPs

Semi-automatic rigs incorporated the embedding of NPs into thermoplastic textiles by the techniques discussed in Section 3.2.3. Characterisation by SEM imaging was employed as a method of assessing the distribution of applied concentration of TiO$_2$ on PET textiles, where a spray-gun was used to apply NPs. A hot-press that was modified with an increased control of temperature to the embedding side, and a non-embedded side that had been sufficiently thermally insulated was employed for the embedding of NPs to textiles. The most stable setting of normalised active temperature, $\tau$ for the hot-press was a value of 0.5. Pull-Off techniques were a method employed to quantify the adhesive strength of NPs to textile. Mapping by EDS was applied as a method of quantifying surface coverage and quality of NP distribution on a surface area of textile. Analytical techniques of AAS were employed to quantify the content of TiO$_2$ (µg/cm$^2$) on textiles, as discussed in Section 3.3.3. Durability testing of NPs to textiles was achieved by employing a laundring standard for effective adherence of NPs to surfaces, as discussed in Section 3.4.2.
5.2.1. Surface Characterisation and Optimisation by Imaging of the Distribution of NPs on PET Fiber Substrates

PET textiles were prepared by spraying TiO$_2$ on surfaces for 2 seconds, employing a value of 0.5 for $\tau$, and 2 min. of clamping by hot-press. Textiles were prepared with varying concentration of TiO$_2$, and the effect of distribution assessed. The applied concentrations of TiO$_2$ were 1, 0.5, 0.25 and 0.15 wt.%. The concentrations were selected based on the outcomes of Section 5.1, preparation of textiles with NPs by manual rigs, where these outcomes highlighted efficient distribution in the region of 1 to 0.15 wt.%.

Figure 5.3 presents a selection of images from textiles prepared with varying concentrations of applied TiO$_2$ (wt.%).

The uneven distribution of NPs over surfaces was permitted when high concentrations of TiO$_2$ were applied, as highlighted by the white shaded areas on fiber surfaces, as presented in Figure 5.3(a). Large agglomeration of NPs was present on the textile surface, as a film when the applied concentrations were between 1 to 0.5 wt.%, Figure 5.3(b). These agglomerates were considered a surface film that does substantially reduce the efficiency of the SA/V of NPs, and has been reported in previous work of TiO$_2$ coated on polymeric substrates [161].

Agglomeration of NPs formed a film at the fiber boundaries and crevices. This film would permit a reduction of breathability and flexibility of the textile, as presented in Figure 5.3(b). The film would also be highly exposed to large scales of damage and subsequently low adherence to the textile surface, as it was effectively a surface coating and not a dispersion of NPs. Stress and flexural movement of the textile would generate a peel of the film, leading to removal of NPs and exposure of large areas of the textile surface, Figure 5.3(c). Large agglomerates can be easily dislodged from the textile surface when subjected to abrasion or liquid contact, and eventual exposure of the textile to microbe colonisation and create a potential cytotoxicity issue [4, 5, 126].

Imaging of textiles that were processed by the semi-automatic rig, using a high concentration of TiO$_2$, permitted similar outcomes to textiles that were processed by the manual embedding rig that was discussed in Section 5.1. The reduction of continuity when distributing NPs over the fibers of the textile was observed, where exposed areas of textile were permitted, as presented in Figure
5.3(d). Formation of a film on fibers was highlighted, and large agglomeration was viewed. As the applied concentration reduced to 0.25 and 0.15 wt.%, a smaller film and reduced sizes of agglomerates were distributed on the fiber surface, Figure 5.3(e). Efficient distribution of NPs was present, while areas displaying a reduced presence of NPs remained, as highlighted. Boundaries between fibers had low quantities of lodged NPs and formations of film, Figure 5.3(f). NPs were finely distributed as individual particles over the fiber surface, with a minimal formation of NP film permitted on the surface. In this instance for example, if NPs were dislodged from the fiber surface, only a low surface area of fiber exposing the PET substrate would be available for microbial attack, as only individual or small agglomerates were dislodged from the surface and not a film of NPs. The surface area exposed was reduced as a result of the individual distribution of NPs, and therefore best utilising the efficiency of the SA/V properties of NPs.

Figure 5.3 SEM images of PET textiles with TiO$_2$ NPs prepared by semi-automatic embedding techniques, 1 wt.% of applied concentration (a&b), 0.5 wt.% (c&d), 0.25 wt.% (e), and 0.15 wt.% (f).
5.2.2. *Quantification of TiO₂ Coverage on PET Textiles by Mapping*

Mapping by EDS techniques was performed on PET textiles applied with TiO₂ by spraying for 2 sec., using a 0.5 value for τ, for a clamping time of 2 min. by hot-pressing. The applied concentrations of TiO₂ were 0.13 and 0.25 wt.%. This range of concentration was selected based on the outcomes from textile characterised by imaging in the previous Section 5.2.1, where the reduction of concentration permitted increasing efficiency of distribution of NPs on surfaces. Spectrum analysis confirmed the presence of Ti by highlighting with a red dot for every NP encountered. The coverage of varying applied concentration of TiO₂ (%) was assessed using selected mapping images, as presented in Figure 5.4. Three replicates of PET textile that were embedded with TiO₂ were prepared by semi-automatic rigs. Mapping proved to be an effective method of analysing the quality and quantity of coverage of Ti on surfaces.

Mapping enabled a quantification of Ti (%) distribution on surfaces, for three random specimens of each replicate, and three random points of interest (POI) on each section. The average data of 27 POI and standard deviation was presented in Figure 5.4. Three textile specimens were mounted on each SEM holding stub of 20 mm. Stubs were coated by gold sputtering for 1.5 minutes, and 10 kV was initiated by the SEM using a resolution of 2 K by imaging.

Textiles prepared with a concentration of 0.13 wt.% had an average coverage of 17% on surfaces. A concentration of 0.25 wt.% permitted increased coverage of the textile surface, 24%. The quantitative analysis of Ti present on textiles correlated with the surface characterisation achieved by imaging using mapping, as presented in Figure 5.4(a-d). The larger coverage of Ti on textiles using a concentration of 0.25 wt.% of TiO₂ was attributed to the densely populated areas of NPs. The highly populated areas of NPs were mostly present at the fiber boundaries and in the voids between fibers, as highlighted in Figure 5.4(c&d). A Related t-test was applied for the difference in effective concentration, and yielded statistically insignificant results as *P* > 0.05. Hence, the null hypothesis that a difference between data collated using 0.13 and 0.25 wt.% exists for the applied concentration, was rejected.
The standard deviations of coverage of Ti on textiles were examined. PET prepared with an applied concentration of 0.13 wt.% had a standard deviation of ± 6%, while a concentration of 0.25 wt.% had ± 10%. The larger standard deviation for the increased concentration indicated a larger fluctuation in surface area coverage of NPS on the textile. This correlates with surface characterisation by imaging of textile surfaces that were applied with low concentrations of TiO₂ by manual embedding rigs, as discussed in Section 5.1. Mapping has enhanced suitability to a qualitative method of analysing surface coverage of NPs on surfaces, instead of using it as a quantitative method.

Imaging textiles prepared with applied concentrations of 0.13 and 0.25 wt.% of TiO₂ by EDS techniques were presented in Figure 5.4(a-d). A finer distribution of NPs on textiles was observed when 0.13 wt.% was applied, as presented in Figure 5.4(a&b), compared to textiles applied with a concentration of 0.25 wt.%, as presented in Figure 5.4(c&d). The reduction of the applied concentration permitted the distribution of NPs in small agglomerates on the fiber surfaces. A reduced presence of large agglomerates and the formation of film on fibers were noted, as presented in Figure 5.4(a). Densely populated areas of Ti were detected in highlighted areas, Figure 5.4(b). Charging effects from the SEM on PET can affect Ti detection [75, 199]. An example of charging was highlighted by the unregistered detection of areas of Ti coverage, Figure 5.4(d). Textile fibers have an inherent roughness and shape, due to the warp and weft patterning of the yarns, which creates distribution effects of electrons that are bombarded by the tungsten filament onto the sample surface [75]. Charging effects on textiles in this study can be attributed to one or all of the following occurrences;

1. Coating thickness of the gold sputtering.
2. An uneven surface on the sample holder.
3. SEM voltage setting was too high.

The application of NPs at an increased concentration of 0.25 wt.%, permitted greater dispersion of NPs on the textile surface, Figure 5.4(c). A large area of Ti was distributed on the fibers, where NPs were adhered to all areas of the fiber surfaces, Figure 5.4(b). A larger presence of Ti agglomeration was observed compared to textiles applied with a concentration of 0.13 wt.%. This was specifically in areas
where ridges of fibers or voids were present at the fiber boundaries, Figure 5.4(c). Within these voids and boundaries, a film formed over the fibers. Large agglomeration of NPs was permitted at these boundaries, as highlighted in Figure 5.4(d). Solute of TiO$_2$ when sprayed may have flowed through the fiber voids, therefore initiating agglomeration of NPs in these zones before the hot-press was applied to the textile surface. When increasing concentrations were applied, it was noted that growth of such films originated in these voids and boundaries.

![Figure 5.4 Ti percentage coverage quantified by EDS mapping on PET textiles prepared by semi-automatic embedding techniques with applied concentrations of 0.13 and 0.25 wt.% of TiO$_2$. EDS mapping of PET fibers with TiO$_2$ distributed over the PET textile fiber surfaces, employing concentrations of TiO$_2$, 0.13 wt.% (a&b), and 0.25 wt.% (c&d).](image-url)
5.2.3. Analysis of the Adherence of NPs to Textiles by Pull-Off Testing

The adhesive strength of TiO$_2$-NPs to PET textiles was analysed by a modified standard for testing adhesion of coatings. “Pull-Off Strength of Coatings Using Portable Adhesion Testers” was a standard test method [211], and modifications applied to this test were discussed in Section 3.4.1. The practical adhesion in this analysis was expressed in the form of tensile strength (force per unit area) of the adhesive-tape, or adhere that was pulled in a perpendicular direction to the textile surface, or the adherend. The force, $P$ was assessed by Eq. 5-1:

$$P = \sigma A$$  \hspace{1cm} \text{(5-1)}

Where, $\sigma$ was the applied stress (MPa) and, $A$ the surface area ($\text{m}^2$) of the dollie applied to the textile surface. The tensile stress of the adhering system was dependent on the rate of pull.

Benchmarking of the standard ASTM D4541-09 was achieved on coated and uncoated sheeting of PVC and textiles of PET, where sample numbers were provided in Table 5.1. Plain PVC and PET textiles with no coating also had a dollie applied to surfaces and were tested for Pull-Off strength. PVC and PET that were coated with TiO$_2$ were prepared with a high concentration of 0.5 wt.% for immobilisation of large quantities of NPs on surfaces. PVC/Ti and PET/Ti samples were prepared by semi-automatic rigs, where the concentration of TiO$_2$ was applied for 2 seconds, and hot-press clamping time for 2 minutes. PVC/Ti and PET/Ti were hot-pressed using a 0.5 value for $\tau$.

<table>
<thead>
<tr>
<th>Material</th>
<th>Coating</th>
<th>Sample No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>None</td>
<td>PVC</td>
</tr>
<tr>
<td></td>
<td>Semi-auto</td>
<td>PVC/Ti</td>
</tr>
<tr>
<td>PET</td>
<td>None</td>
<td>PET</td>
</tr>
<tr>
<td></td>
<td>Semi-auto</td>
<td>PET/Ti</td>
</tr>
</tbody>
</table>

Table 5.1 Sample number of Pull-Off test benchmarking surfaces for PET and PVC surfaces
Samples PVC, PET, PVC/Ti and PET/Ti were tested for the dollie *Pull-Off* strength. The adhesion tester was operated to destruction, where the dollie pulled away from the surface, where 6 replicate of each sample was achieved. The average data calculated by the adhesion tester was the arithmetic mean of the force readings of 6 tensile data outputs with standard deviation applied, as presented in Figure 5.5.

The outcomes of *Pull-Off* testing were presented in Figure 5.5. Sample PVC/Ti had an average *Pull-Off* force of 102 N, and PVC 108 N. PET had an average *Pull-Off* force of 38 N, also 6 N less than PET/Ti had, where its *Pull-Off* force was 44 N. The differences of *Pull-Off* force between PVC based surfaces, and PET based surfaces was attributed to the contact surface areas of the dollie, and the increased surface roughness of the PET textiles. PVC surfaces have a larger surface area of contact with the dollie, when compared to PET textiles. The increased PVC surface area was due to the non-porous nature of PVC, compared to PET having 45% porosity, as measured by imaging. Where the PET textile had 45% porosity, and a larger surface roughness due to the warp and weft patterning of the fibers, a reduced surface area of contact with the dollie existed, as described by the schematic illustration in Figure 5.5.

The outcomes indicate a difference between the *Pull-Off* force for coated and uncoated PVC with coated and uncoated PET surfaces, as presented in Figure 5.5. A difference in the *Pull-Off* data between PVC and PVC/Ti surfaces yielded statistically insignificant results, as $P > 0.05$. A difference in *Pull-Off* data between PET and PET/Ti textiles also yielded statistically insignificant results, as $P > 0.05$. Hence, the null hypothesis that a difference between *Pull-Off* forces existed between coated and uncoated surfaces of PVC and PET was rejected. Therefore, direct measurement of adhesion of NPs to surfaces cannot be quantified by *Pull-Off* testing.
An indirect method of quantifying the adhesion of NPs to textile surfaces was tested. It was achieved by analysing the TiO$_2$ present on the adhesive-tape applied to the dollie for Pull-Off testing. The tensile force required to detach a dollie from a material surface can be employed as a pass/fail benchmark for Pull-Off testing. For example, in the case that a Pull-Off test did not exceed a benchmark tensile force, the resultant adhesive-tape was discarded, and the test was repeated. In this study, the benchmark force for PET textiles was set according to data from Figure 5.5, where the force was 38 ±6 N. The location of the dollie position on the material surface was recorded, and the adhesive-tape was removed from the dollie and preserved, as presented in Figure 5.6(d).

PET textiles were sprayed for 2 sec. with a concentration of 1 and 0.5 wt.% of TiO$_2$, using 0.5 value for $\tau$, and clamping the hot-press on textiles for 2, 4, 6 and 8 minutes. The specimens analysed were: the adhesive-tape after the destruction test;
the PET textile surface where the adhesive-tape had been removed: and a specimen of undamaged PET textile surface coated with TiO₂. Sample numbers are listed in Table 5.2. Sample numbers are distinguished by: textile material (Mat); embedding technique (Tech); applied concentration (Con); and clamping time of the hot-press (Tim).

Table 5.2 Coding system of PET textile, displaying embedding technique, concentrations of TiO₂ and clamping time of hot-press.

<table>
<thead>
<tr>
<th>Material</th>
<th>Technique</th>
<th>Concentration (wt.%)</th>
<th>Clamping time (min.)</th>
<th>Sample No. Mat/Tech/Conc/Tim</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Semi-Auto</td>
<td>1</td>
<td>2</td>
<td>PET/SA/1/2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>PET/SA/1/4</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>6</td>
<td>PET/SA/1/6</td>
</tr>
<tr>
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<td></td>
<td>8</td>
<td>PET/SA/1/8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>2</td>
<td>PET/SA/0.5/2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>PET/SA/0.5/4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>PET/SA/0.5/6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td>PET/SA/0.5/8</td>
</tr>
</tbody>
</table>

A lower stress yielded a failure of the Pull-Off test, and higher value of stress yielded a pass. The average outcomes were the arithmetic mean of Ti (%) versus Au (%) present on stubs that were gold sputtered, for two replicates of each sample. Specimens were individually placed on a 20 mm aluminium stubs for the SEM, and coated by gold sputtering for 1.5 minutes. The SEM voltage was set at 12 kV and a magnification of 35 X, this been an optimised setting for mapping by EDS, as presented in Figure 5.6(a-c). The specimens of adhesive-tape that were characterised by the EDS, display a warp and weft patterning on the surfaces, as presented by imaging in Figure 5.6(a&b). These patterns were imprints of PET fibers, where the adhesive-tape had been adhered. The highlighted bright white regions were confirmed by EDS peaks to consist of Ti, Figure 5.6(c). Sample PET/1/4 permitted large quantities of Ti on its surface, specifically in highlighted areas. The dislodgement of Ti was initiated most often in areas where the warp fibres passed over the weft fibers. This indicated a large presence of Ti situated at these areas, and that NPs were inefficiently distributed over the surface. It was noted during Pull-Off testing that the adhesive-tape made increasing contact at areas where the warp and
weft fibers passed over and under each other, therefore enabling an increased contacting surface with Ti. Here the textile was at its largest depth, and initiating the point of first contact with the adhesive-tape, as presented in Figure 5.6(e). The specimens of adhesive-tape from sample PET/0.5/4 permitted a reduced presence of bright white imprints. This indicated that textiles clamped by the hot-press for a longer duration and a reduced applied concentration provided lower quantities of NPs on the surface of the adhesive-tape, as displayed in Figure 5.6(b).

![Figure 5.6 Imaging of EDS mapping, PET/1/4 adhesive-tape (a), PET/0.5/4 adhesive-tape (b), PET/1/4 EDS analysis (c), EDS mapping samples of adhesive-tape fabric, before and after Pull-Off testing (d), and warp and weft point of contact with adhesive-tape on the dollie (e).](image)

The specimens assessed included: Ti (%) permitted on adhesive-tape after destruction by the adhesion tester; the Ti on PET textiles before Pull-Off testing; and the Ti on PET textiles after Pull-Off testing. These specimens were compared against Au (%), as presented by the graphs in Figure 5.7, where EDS data was supplied in ‘Appendix C’. Sample PET/1/2 had coverage of 8% of Ti on adhesive-tape surfaces after Pull-Off testing, and coverage of 68% of Ti on PET textile surfaces after Pull-
Off testing. The coverage of Ti on adhesive-tape when added to the coverage on textiles after Pull-Off testing permitted a total of 76% of Ti. There was similar coverage on PET undamaged by Pull-Off testing, 77%. Coverage of Ti increased on adhesive-tape with increasing clamping times of the hot-press, from 2 to 6 minutes. Sample PET/1/4 and PET/1/6 permitted a reduction of coverage of Ti on PET textiles after Pull-Off testing, compared to undamaged PET before Pull-Off testing. Sample PET/1/4 and PET/1/6 also permitted less coverage of Ti than sample PET/1/2. Standard deviations of data collated present no significant difference of coverage of Ti between samples PET/1/2 and PET/1/4 for adhesive-tape surfaces, undamaged PET textiles, and PET textiles after Pull-Off testing. Sample PET/1/8 had the lowest coverage of Ti on adhesive-tape surfaces and PET textiles before and after Pull-Off testing. Coverage of Ti on textiles after hot-pressing was 50%, which was considerably lower than PET textiles prepared with shorter clamping times of the hot-press. The reduced coverage was assumed to be a factor of the inconsistency of the manual spraying of TiO₂ on textiles. The variation of coverage of Ti was 10% for surfaces of PET after hot-pressing, which was a significant difference.

Figure 5.7 Percentage of Ti versus Au determined using the EDS mapping technique, on samples PET/1/2, PET/1/4, PET/1/6 and PET/1/8 after Pull-Off testing.
The coverage of Ti versus Au (%) on PET textiles prepared with an applied concentration of 0.5 wt.% of TiO$_2$ were presented in Figure 5.8. Sample PET/0.5/2 had 10%, 39% and 29% coverage of Ti on adhesive-tape surfaces, undamaged PET textiles, and PET textiles after Pull-Off testing, respectively. These outcomes correlate where the adhesive-tape and the PET textile after Pull-Off testing were added together (39%), the outcome achieved the same coverage of Ti (%) as the undamaged PET textile had before Pull-Off testing, 39%. Sample PET/0.5/4 had a low coverage of Ti, below 20%, with 3% permitted on adhesive-tape. Sample PET/0.5/6 permitted an increasing Ti coverage, 38% on PET after Pull-Off testing, more than PET before Pull-Off testing, 26%. These outcomes indicated inconsistencies with the mapping technique of quantifying coverage of Ti on surfaces, as the maximum coverage of Ti that can be permitted on surfaces after Pull-Off testing can be 100% of Ti that is permitted on surfaces before Pull-Off testing. In this case, 26% coverage of Ti on PET before Pull-Off testing was less than 38% of coverage after Pull-Off testing.

The variation in outcomes was attributed to the method of application of TiO$_2$ to the textile surface by manual spraying of TiO$_2$ with a spray-gun. The adhesive-tape from sample PET/0.5/6 also had large coverage of Ti (%). When this coverage was added to PET textiles after Pull-Off testing, the outcome indicated a large inconsistency in the method of testing and preparation of PET textiles by semi-automatic rigs. Sample PET/0.5/8 presented low quantities of Ti (%) on the adhesive-tape surface, 3% indicating the adherence of NPs on PET when a long duration of hot-pressing was employed. The longer hot-press time permitted the non-embedded side of the textile to reach increasing temperatures. This action reduced a temperature barrier that existed between the hot-press and the textile surface which was attached to the steel holder. The steel holder had a high thermal conductivity, and therefore dissipated heat from the hot-press side more readily. With longer clamping times the steel plate increased in temperature, and permitted the hot-press to stabilise in temperature.

The applied concentration had an effect on the coverage of Ti (%) permitted on PET textiles, where textiles applied with 1 wt.% of TiO$_2$ had in the region of 55 to 80%, and 0.5 wt.% had 20 to 40% of coverage on surfaces. A high concentration
permitted a larger presence of Ti (%) on adhesive-tape, indicating the reduced adherence of TiO$_2$ to the PET. The duration of clamping time had a significant effect, where the coverage of Ti (%) on undamaged textiles before Pull-Off testing reduced with an increasing clamping time of the hot-press, as presented by the outcomes in Figure 5.7 and Figure 5.8.

![Figure 5.8 Percentage Ti versus Au quantified by mapping, on specimens after Pull-Off testing. PET textiles were prepared by semi-automatic techniques, using an applied concentration of 0.5 wt.% of TiO$_2$.](image)

The samples of adhesive-tape, fabric, and pull-test fabric were analysed by AAS techniques for quantification of TiO$_2$ content, as per methods discussed in Section 3.4.1. The data output of TiO$_2$ (mg/l) by AAS from samples of adhesive-tape was zero, and therefore, no significant measurement of adhesion could be derived, even when 12 samples of adhesive-tape were saturated in HF solution.

5.2.4. Assessment of the Durability of NPs to Textiles by Cycles of Laundering

PET textiles were prepared with concentrations of 0.5 and 0.15 wt.% of TiO$_2$ by manually spraying textiles for 2 sec. Textiles were clamped with the hot-press for 3 and 0.5 minutes, using 0.13 and 0.5 for a value of $\tau$. Laundering of textiles was
employed as a method of testing the durability of NPs to PET textiles. Textiles were prepared and laundered according to techniques detailed in Section 3.4.2. Ti (mg/l) content was measured by employing AAS techniques, as described in Section 3.3.3. The content of Ti on textiles was quantified after 0, 1 and 10 cycles of laundering. The parameters employed for the preparation of textiles with TiO$_2$ were listed with respective samples numbers in Table 5.3. Sample numbers are distinguished by: textile material (Mat); embedding technique (Tech); applied concentration (Con); clamping time of hot-pressing (Tim); and the normalised active temperature of the hot-press ($\tau$).

<table>
<thead>
<tr>
<th>Material</th>
<th>Embedding Technique</th>
<th>Concentration (wt.%)</th>
<th>Clamping time (min.)</th>
<th>$\tau$</th>
<th>Sample No. Mat/Tech/Con/Tim/$\tau$</th>
</tr>
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<tbody>
<tr>
<td>PET</td>
<td>Semi-Auto (SA)</td>
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<td>0.5</td>
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</tr>
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<tr>
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<tr>
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<td>PET/SA/0.15/3/0.13</td>
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</tr>
<tr>
<td></td>
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<td></td>
<td>0.5</td>
<td>PET/SA/0.15/3/0.5</td>
<td></td>
</tr>
</tbody>
</table>

The quantity of TiO$_2$ (µg/cm$^2$) retained on samples PET/SA/0.5/0.5/0.13, PET/SA/0.5/3/0.13, PET/SA/0.5/0.5/0.5, and PET/SA/0.5/3/0.5 was presented in Figure 5.9. The retention of TiO$_2$ (%) on these samples after 1 cycle, and between 1 and 10 cycles of laundering, was presented in Figure 5.10.

An initial content of TiO$_2$ between 16 and 19 µg/cm$^2$ was recorded on all textile samples before laundering. Shorter clamping times and hot-press parameters had an effect on the adherence of NPs to textiles, where sample PET/0.5/0.5/0.13 presented a large deviation of content of 15 to 22 µg/cm$^2$ of TiO$_2$ after hot-pressing. Clamping time affected the initial adherence of NPs to PET, after 1 cycle of laundering both samples PET/0.5/0.5/0.5 and PET/0.5/0.5/0.13 permitted 50% and 40% of retention of TiO$_2$ respectively, as presented in Figure 5.10. After 10 cycles,
the content reduced by greater than 50% from measurements after 1 cycle. As both these textiles were prepared with a τ value of 0.13 and 0.5, it can be stated that PET had a low rate of heat transfer with the hot-plate during hot-pressing. This was a result of high thermal conductivity in the system, which was not a feature of the PET textile, but more a feature of the stainless steel plate upon which the PET sample was mounted. Samples PET/0.5/3/0.5 and PET/0.5/3/0.13 permitted the retention of more than 90% of TiO₂ on surfaces after 1 cycle, and permitted low quantities of loose NPs on the textile. After 10 cycles, sample PET/0.5/3/0.5 had 6.5 μg/cm² of content after 10 cycles, which was the largest quantity of TiO₂ on PET after 10 cycles. A large reduction of TiO₂ was noted on samples PET/0.5/3/0.5 and PET/0.5/3/0.13 between 1 and 10 cycles, where retention of 50% and 40% was recorded respectively. The reduction of TiO₂-NPs was both a factor of the large presence of agglomeration and poor embedding of the agglomerates to the textile fibers, as described in Figure 5.9(a). Large agglomerates initiated a film of NPs at the boundaries of fibers. Laundering of textiles initiated the peel and removal of agglomerate films, permitting a substantial loss of content of TiO₂ on the textile, Figure 5.9(b). The increasing value of τ and increasing clamping times of hot-press permitted the increasing efficiency of retention of TiO₂ to PET. This outcome was also highlighted by the Pull-Off test outcomes in Section 5.2.3.
Figure 5.9 TiO\textsubscript{2} retention on PET textiles after cycles of laundering. Textiles with NPs processed by semi-automatic rigs, 0.5 and 3 min. clamping times, τ was 0.5 and 0.13, using PET textiles and concentration of 0.5 wt.\% of TiO\textsubscript{2}. An illustration of the cross sectional view of the NPs embedded into textile fibers, where there is a large presence of NPs before laundering (a), and removal of agglomerates after 10 cycles of laundering (b).

Figure 5.10 The retention of TiO\textsubscript{2} on PET textiles after laundering, prepared by semi-automatic techniques, with 0.5 and 3 minute clamping time, a τ value of 0.5 and 0.13 where the applied concentration was 0.5 wt.\% TiO\textsubscript{2}. 

0-1 Laundering Cycles
* 1-10 Laundering Cycles

PET/0.5/3/0.5
PET/0.5/3/0.13
PET/0.5/0.5/0.5
PET/0.5/0.5/0.13
The quantity of TiO$_2$ ($\mu$g/cm$^2$) at respective cycles of laundering on PET that was prepared using 0.5 and 0.13 values for $\tau$ while employing a concentration of 0.15 wt.% of TiO$_2$ and a clamping hot-press times of 0.5 and 3 min. are presented in Figure 5.11. Retention of TiO$_2$ (%) on samples PET/SA/0.15/0.5/0.13, PET/SA/0.15/3/0.13, PET/SA/0.15/0.5/0.5 and PET/SA/0.15/3/0.5 was quantified after 1 cycle, and between 1 and 10 cycles of laundering, as presented in Figure 5.12.

An initial content of 7 to 8 $\mu$g/cm$^2$ was recorded on all of the PET samples after hot-pressing. All the samples retained over 80% of TiO$_2$ retained after 1 cycle, where sample PET/0.15/0.5/0.13 had the lowest retention of TiO$_2$, 76.3%. This high retention was a result of the low agglomeration of NPs and formation of film at the fiber boundaries. This permitted a reduced surface area of exposure when an agglomerate of NPs was dislodged, as presented in Figure 5.11(a). For example, In the case of a dislodged NP, the minimised effect it had on another NP which it had no contact with was noted. Hot-press setting, $\tau$ had an effect on the retention of TiO$_2$ between 1 and 10 cycles, where samples PET/0.15/0.5/0.13 and PET/0.15/3/0.13 retain 70% of TiO$_2$, or 4 $\mu$g/cm$^2$. The hot-press was of an insufficient temperature to soften the PET for embedding of NPs, permitting dislodgement of poorly embedded NPs, as described by the schematic illustration in Figure 5.11(b). However, due to good distribution of NPs at this concentration, NPs that were efficiently embedded to the textile surface had no effect on neighbouring NPs, as discussed in the previous sections. Samples PET/0.15/0.5/0.5 and PET/0.15/3/0.5 had greater than 90% of TiO$_2$ retained between 1 and 10 cycles, where 6 $\mu$g/cm$^2$ of TiO$_2$ was recorded. These textiles permitted promising outcomes of adhesion of TiO$_2$ to PET textiles.
Figure 5.11 Retention of TiO$_2$ on textiles after cycles of laundering. Textiles were prepared using the semi-automatic embedding technique, with 0.5 and 3 minute hot-press clamping times, and where $\tau$ was 0.5 and 0.13, using a PET textiles and an applied concentration of 0.15 wt.% of TiO$_2$. A schematic illustration displaying the cross sectional view of the NPs embedded into textile fibers, good adhesion of NPs prepared (a), and poor adhesion of NPs to textile fibers (b).
It was evident from samples before laundering, that employing a concentration of 0.5 wt.% of TiO₂ permitted approximately a 50% increase of TiO₂ content on PET compared to PET with 0.15 wt.% of TiO₂. While a longer clamping time proved to permit greater benefit for increasing concentrations after 1 cycle. Increasing the value of \( \tau \) permitted the increasing retention of TiO₂ for reduced concentrations. Employing the semi-automatic rigs, a threshold between 2 and 6 \( \mu \)g/cm² of TiO₂ content on PET after 10 cycles was present. Increasing the value of \( \tau \) proved to be the catalyst for increasing retention of NPs on textiles. Here the PET elastic modulus was reduced, or textile fiber resistance to embedding of NPs. A reduced concentration permitted increasing retention of TiO₂ (%) on PET after laundering. As discussed in previous sections, the increasing concentration created a film of NPs between boundaries of fibers, enabling larger surface areas of agglomeration available for peel and dislodgment from surfaces. This was proven by poor retention of NPs on PET prepared with a concentration of 0.5 wt.%, where the best result, sample PET/0.5/3/0.5, had retention of 35% between 0 and 10 cycles.
5.2.5. Summary

Embedding by semi-automatic rigs of NPs to PET textiles was examined for the applied concentrations of TiO$_2$. Surface characterisation by SEM highlighted formations of a film of NPs on surfaces where high concentrations were applied, 1 wt.% of TiO$_2$. The clustering of large agglomerates of NPs were at the foundation of these films located at the boundaries of fibers. This indicated an inefficient distribution of NPs on the textile surface. Flexural stresses applied to the textile permit a peel of the film from the fibers, thereby exposing large areas of the fiber and permitting an increasing area available for microbial colonisation. A low concentration permitted the individual distribution of NPs on the textile surface. Individual distribution enhances the efficiency of the SA/V of NPS and almost eliminates formation of large agglomerates and the formation of a NP film. Dislodgement of an individual NP has no effect on the potential exposed surface area of the textile. Neighbouring NPs were sufficiently distributed to cover the exposed area left by a dislodged NP.

Mapping by EDS was an imaging technique examined the coverage and placement of specific elements on a specimen. The coverage of TiO$_2$ (%) on PET textiles was quantified for applied concentrations of 0.25 and 0.15 wt.% of TiO$_2$. The outcomes highlight no significant difference between textiles prepared with different concentrations. However, a substantially large deviation in the coverage of TiO$_2$ on textiles prepared with 0.25 wt.% was observed. The textiles presented large agglomeration and subsequent films at the fiber boundaries. Characterisation of images by EDS highlighted the growth of films beginning at the boundaries of fiber boundaries. The fiber boundaries filtered NPs, where NPs then agglomerated more readily with increasing applied concentration.

A modified version of ASTM D4541-09 was applied to PET textiles to examine a suitable method of measuring the adhesion of NPs. The outcomes of the Pull-Off test presented a potential novel method to measure adhesion of NPs to PET textiles. Measurements of force from the Pull-Off test required the dislodgement of a dollie fitted with an adhesive-tape, and had no significant results for measurement of adhesion of NPs. The force measurements were therefore employed as a benchmark pass/fail test. For example, in the case of a dislodged dollie from a textile specimen
below the benchmark fail level, the test was repeated. The coverage of Ti quantified by mapping was achieved on specimens of adhesive-tape, and PET textiles before and after Pull-Off testing. The outcomes highlight the inconsistent distribution of TiO$_2$ by a manually operated spray-gun. The technique of manually applying TiO$_2$ by spray-gun was reliant on the consistency and quality of the operator.

Analytical techniques by AAS were a successful method employed to quantify the content of Ti (mg/l) on PET textiles, which was then converted to units of TiO$_2$ ($\mu$g/cm$^2$). Laundering of textiles prepared by semi-automatic rigs provided a novel method of testing the durability of NPs to textiles. Low applied concentrations of TiO$_2$, high parameters of $\tau$, and longer clamping times permitted the most efficient retention of TiO$_2$ after 10 cycles of laundering.

5.3. Embedding of NPs to Textile Surfaces by Automatic Rigs

Embedding of NPs to textiles by automatic rigs was achieved using the techniques discussed in Section 3.2.4. The velocity of the calender roller was set at an optimum linear velocity of 3 mm/sec. A calender roller of two variations with different thermal conductivities was employed during this study. Surface characterisation by SEM was employed to optimise the distribution of TiO$_2$-NPs on PET textiles by varying the applied concentrations to the surface. The textiles were subjected to cycles of laundering as a method of evaluating the durability of NPs to the textiles, as discussed in Section 3.4.2. Analytical techniques by AAS were employed to quantify the content of TiO$_2$ ($\mu$g/cm$^2$) on textile surfaces. Furthermore, the applicability of the embedding technique was extended to incorporate TiO$_2$-NPs to surfaces of acrylic and CA thermoplastic textiles. A coding system was provided, with a list of the thermoplastic textiles prepared by automatic rigs, and was presented in Table 5.4. Sample numbers were categorised by: textile material (Mat); embedding rig (Tech); material surface of calender roller (Roll); applied concentration (Conc); and the normalised hot-press active temperature ($\tau$).
Table 5.4 Coding system displaying textile material, embedding technique, applied concentration of TiO$_2$ and hot-press temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Embedding Technique</th>
<th>Calender Roller</th>
<th>Applied Concentration (wt.%)</th>
<th>( \tau )</th>
<th>Sample No. Mat/Tech/Roll/Conc/( \tau )</th>
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5.3.1. Embedding of NPs to Textiles by Automatic Rigs Fitted with a Stainless Steel Calender Roller

PET textiles were prepared by automatic rigs fitted with a stainless steel calender roller, as discussed in Section 3.3.4. Imaging by SEM of PET textiles processed with the automatic rigs were presented in Figure 5.13. A hot-press setting, \( \tau \) was employed, where the setting was stable during automatic embedding of textiles and optimised based on the outcomes from manual embedding rigs in Section 5.1. Concentrations of 0.5 and 0.15 wt.% of TiO$_2$ were applied to textiles. The applied concentrations were selected by the outcomes of semi-automatic embedding of textiles in Section 5.2.
The surface of textile sample PET/AT/S/0.5/0.7 displayed a large presence of TiO$_2$ on fibers, as presented in Figure 5.13(a). A consistent distribution of NPs on the fiber surface was observed, with partial agglomeration of NPs and formation of a NP films at the boundaries of fibers, as highlighted in Figure 5.13(a). It was noted that an uneven distribution of NPs was present, as the distribution permitted densely agglomerated areas on the surface, as presented in Figure 5.13(b). After 1 cycle of laundering, the loosely adhered NPs and agglomerates were dislodged from the fibers, as highlighted in Figure 5.13(c). NPs that were finely distributed were clearly visible, displaying good distribution on fibers. On analysis of imaging by higher resolutions, it was observed that the NPs had formed small agglomerates with an approximate width of 0.5 to 2 µm on fibers, as highlighted in Figure 5.13(d). The agglomerate sizes equated to an approximate quantity of 10 to 40 NPs. A large presence of agglomeration of NPs was observed, where the agglomerates were distanced 2 µm from neighbouring agglomerates, as presented in Figure 5.13(d). This distribution permitted efficient use of the SA/V of TiO$_2$-NPs, where the maximum fiber coverage was achieved for a minimal quantity of NPs.

The large agglomerates on surfaces were dislodged after 10 cycles of laundering, as presented in Figure 5.13(e). Finely dispersed NPs were efficiently distributed over the textile, with no agglomeration permitted at the fiber boundaries. It was noted that small anomalies were observed on fibers, as highlighted by the green markers, and were retained on textiles during the laundering. Analysis of the anomalies by EDS spectrum permitted detection of silicon, which was a base material in the laundering detergent employed. Small agglomerates of NPs were still permitted on the fiber surface as viewed under high magnification, where sizes recorded were 0.5 to 1 µm, as presented in Figure 5.13(f).
Characterisation by imaging of sample PET/AT/S/0.15/0.7 was presented in Figure 5.14. A large presence of NPs on PET was observed, permitting a low presence of agglomeration and formations of film at boundaries of fibers, Figure 5.14(a). Agglomerates of NPs were permitted on the surface of fibers that were exposed to the hot-plate, as highlighted in Figure 5.14(a). A homogeneous distribution of finely dispersed and adhered NPs was permitted on fibers, as presented in Figure 5.14(b). The reduced concentration of the applied TiO₂ had initiated this distribution effect of NPs. Loosely adhered NPs to fiber surfaces were dislodged after the first cycle of laundering, as viewed by the exposed fiber surface.
in Figure 5.14(c). Agglomeration of NPs and the formation of film were not present at fiber boundaries. NPs were finely distributed in agglomerate sizes of 0.5 to 1 µm, as presented in Figure 5.14(d). After 10 cycles there were no large agglomerates of NPs present on fibers, Figure 5.14(e). Characterisation of samples under high magnification presented densely populated areas of agglomeration of NPs, where an inconsistent distribution was permitted on fibers, as presented in Figure 5.14(f). Laundering of textiles for up to 10 cycles had proved too robust for and increasingly tested the durability of NPs to PET textile fibers, where NPs were dislodged due to abrasion from water flow, and fabric to fabric contact during the laundering process.

Figure 5.14 SEM imaging, plan view of sample PET/AT/S/0.15/0.7 prepared by automatic techniques, using a stainless steel calendar roller, and τ value of 0.7, with a concentration of 0.15 wt.% TiO₂, at 0 cycles of laundering (a&b), 1 cycle (c&d), and 10 cycles (e&f).
The effect of applied concentration of TiO$_2$ on the distribution of NPs and subsequent adherence to textile surfaces was achieved quantifying the content of TiO$_2$ (µg/cm$^2$) present on textiles after 0, 1 and 10 cycles of laundering, as presented in Figure 5.15. The quantified TiO$_2$ (%) retained on PET after 10 cycles of laundering was presented in Figure 5.16. Textiles were prepared as detailed in Section 3.3.2, using a textile transfer velocity of 3 mm/sec. Characterisation by SEM was achieved on PET textiles applied with concentrations of 0.5, 0.25, 0.15 and 0.06 wt.% of TiO$_2$. The hot-press was employed at the optimised setting for PET textiles, where a $\tau$ value of 0.7 was initiated. This setting was an optimised setting from the outcomes of manual and semi-automatic rigs discussed in Sections 5.3.1 and 5.3.2.

Sample PET/AT/S/0.5/0.7 had an initial TiO$_2$ content of 36 µg/cm$^2$ on PET after automatic embedding by rigs, as presented in Figure 5.15. The total content present had a large variation, ±4 µg/cm$^2$, indicating an inconsistency of the distribution of TiO$_2$ during the spraying step of the process. After 1 cycle, only 50% of NPs were retained on sample PET/AT/S/0.15/0.7, and after 10 cycles this was reduced to a value of 10 µg/cm$^2$. The trend correlated with outcomes from surface characterisation by imaging, as presented in Figure 5.13, where large agglomerates of NPs were dislodged from the textile after laundering. Sample PET/AT/S/0.25/0.7 had 16.7 µg/cm$^2$ on PET surfaces, less than half that PET/AT/S/0.5/0.7 had after embedding. PET/AT/S/0.25/0.7 retained greater than 70% retention after 1 and 10 cycles, where content retained was 9 µg/cm$^2$. The low deviations of TiO$_2$ present on sample PET/AT/S/0.25/0.7 indicated an efficient and homogeneous distribution of NPs on surfaces. Sample PET/AT/S/0.15/0.7 had a similar quantity of content and retention to sample PET/AT/S/0.25/0.7, where 16.3 µg/cm$^2$ was retained before laundering and 8.1 µg/cm$^2$ was present on after 10 cycles. These outcomes correlated with surface characterisation by imaging presented in Figure 5.14, where a low distribution of NPs was permitted. After 10 cycles the smaller sized agglomerates were retained on surfaces. Sample PET/AT/S/0.06/0.7 had an initial content of 11.7 µg/cm$^2$ and retained 76% of this value after 1 cycle and 67% after 10 cycles, where a final content of 6 µg/cm$^2$ of TiO$_2$ was present.
Figure 5.15 TiO$_2$ (µg/cm$^2$) on textiles after cycles of laundering. Textiles were prepared using the automatic embedding technique with a 3 m/s textile transfer velocity, and $\tau$ value of 0.7 initialised with PET and a concentration of 0.5, 0.25, 0.15 and 0.06 wt.% of TiO$_2$ using a steel calender roller.

Figure 5.16 Retention of TiO$_2$ on PET textiles after 10 cycles of laundering, prepared by automatic embedding techniques, with a 3 m/s textile transfer velocity, and $\tau$ value of 0.7 initialised with PET and a concentration of 0.5, 0.25, 0.15 and 0.06 wt.% TiO$_2$.

Samples PET/AT/S/0.25/0.7, PET/AT/S/0.15/0.7 and PET/AT/S/0.06/0.7 had a low deviation of TiO$_2$ present on surfaces, ± 1 µg/cm$^2$. The low deviation indicated that efficient control of distribution of NPs on textile surfaces was achieved when the applied concentration was lower than 0.5 wt.% of TiO$_2$. The large deviation of content of TiO$_2$ achieved for sample PET/AT/S/0.5/0.7 was a result of the filtering of
NPs at the fiber boundaries. On spraying of the solute of TiO$_2$ to the textiles, the fibers act as filters where the natural instinct of the solute was to try and flow through the fibers, thereby acting as a filter of NPs and initiating agglomeration. As discussed in Section 5.2, an increasing applied concentration correlated with the increasing size of agglomerates, where NPs were increasingly filtered at the fiber boundaries, due to increasing size.

Inefficiently adhered NPs were quantified by the retention of NPs permitted on textiles after 1 cycle of laundering. The durability of NPs permitted on textile surfaces was achieved after 10 cycles. The effective outcomes of clamping time and value of $\tau$ on the adherence of NPs was discussed in Section 5.2.3. The outcomes highlight the high thermal conductivity of the stainless steel holder of textiles, and the subsequent negative effect it had on the heat transfer between the hot-plate and textile surface during hot-pressing. The steel holder created a large temperature barrier with the hot-press, where heat was dissipated away from the hot-press side and permitting a lower surface temperature of the textile then required for efficient embedding of NPs.

5.3.2. Embedding of NPs to PET Textiles by Automatic Rigs fitted with a Cotton Calender Roller

The outcomes of previous sections have highlighted the importance of the non-embedding side, specifically the negative effect that the high thermal conductivity has during heating of the embedding side of the textile. A stainless steel calender roller with a high thermal conductivity used in Section 5.3.1, was replaced by a cotton calender roller of lower thermal conductivity, as described in Section 3.2.4. The adherence and distribution of NPs on PET textiles was achieved for parameters of applied concentration of TiO$_2$ and values of $\tau$. Content of TiO$_2$ permitted on PET textiles was quantified by analytical techniques of AAS, where NPs were tested for durability to textiles at cycles of 0, 1, 10 and 40 of laundering.
5.3.2.1. Effect of the Hot-Press Active Temperature on the Adherence of TiO₂ to PET Textiles after Cycles of Laundering

The effective values of $\tau$ on the durability of TiO₂ to PET textiles were presented in Figure 5.17. Textiles were prepared using a $\tau$ value of 0.1, 0.4, 0.6 and 0.7. Outcomes already discussed in Section 5.3 indicated that 0.25 wt.% of TiO₂ was an optimum applied concentration of spray to textiles for efficient distribution of NPs on surfaces. The data collated for the content of TiO₂ on sample PET/AT/C/0.5/0.1 after various cycles of laundering was presented in Figure 5.17(a).

An initial content of 15 µg/cm² was observed before laundering, with minimal deviation from the mean, ± 2 µg/cm². Inefficiently adhered NPs were dislodged from the textile surface after 1 cycle of laundering, where TiO₂ content retained was 10 µg/cm². After 10 and 40 cycles of laundering, 7 and 5.5 µg/cm² of TiO₂ was retained respectively. Sample PET/AT/C/0.5/0.4 had an initial content of 16.4 µg/cm², was presented in Figure 5.17(b). After 1 cycle, 11.1 µg/cm² was retained on textiles. This reduced to 7.7 µg/cm² after 10 cycles, and 6.8 µg/cm² was retained between 10 and 40 cycles. Increasing the value of $\tau$ indicates the presence of an increasing content of NPs, where sample PET/AT/C/0.5/0.6 had 20.6 µg/cm², as presented in Figure 5.17(c). A large dislodgment of NPs after 1 cycle was noted, 11.1 µg/cm². The increasing adherence of NPs was observed on sample PET/AT/C/0.5/0.6, compared to sample PET/AT/C/0.5/0.4, where 7.3 µg/cm² was retained after 40 cycles. The largest presence of TiO₂ before laundering was observed on sample PET/AT/C/0.5/0.7, 20.5 µg/cm², as presented in Figure 5.17(d). Retention of 80% of TiO₂ was noted after 1 cycle, giving a value of 17 µg/cm², where loosely adhered NPs were dislodged from the textile. The increasing value of $\tau$ permitted an increase of the adherence of NPs to textiles. After 10 and 40 cycles of laundering, 13.6 and 12.7 µg/cm² was retained respectively. These outcomes indicate the significant retention of TiO₂ on textiles between 10 and 40 cycles for sample PET/AT/C/0.5/0.7. The retention of TiO₂ on textiles after cycles of laundering initiates a logarithmic relationship, as viewed by the black lines in Figure 5.17(a-d).
Figure 5.17 TiO$_2$ (µg/cm$^2$) on PET textiles after cycles of laundering, using the automatic embedding technique, employing an applied concentration of 0.25 wt.% of TiO$_2$, a 3 m/s textile transfer velocity, and a $\tau$ value of 0.1 to 0.7. Sample No. a: PET/AT/C/0.25/0.1; b: PET/AT/C/0.25/0.4; c: PET/AT/C/0.25/0.6; d: PET/AT/C/0.25/0.7.
5.3.2.2. Effect of Applied Concentration of Spray on the Adherence of TiO$_2$ to PET Textiles after Cycles of Laundering

The effective variation of the applied concentration of TiO$_2$ to PET textiles was presented in Figure 5.18 to Figure 5.21. PET textiles were prepared with applied concentrations of 0.5, 0.25, 0.15 and 0.06 wt.% of TiO$_2$. The outcomes of Section 5.3.2 indicated that a $\tau$ setting of 0.7 provided the optimum efficiency of for adherence of NPs to PET textiles during durability testing. Sample PET/AT/C/0.5/0.7 had the largest applied concentration of 0.5 wt.% to textiles. An initial content of TiO$_2$ permitted on textiles was 30 $\mu$g/cm$^2$. There was a minimal deviation, $\pm$1.4 $\mu$g/cm$^2$ on textiles before laundering, as presented in Figure 5.18. Retention of 60% of TiO$_2$ was noted after the loosely adhered NPs were dislodged by the first laundering cycle, where 18.2 $\mu$g/cm$^2$ was retained on textiles. Content of 12.6 $\mu$g/cm$^2$ was retained after 10 cycles, where retention of 60% was observed between the 1 to 10 cycles of laundering. After 40 cycles of laundering, 11.2 $\mu$g/cm$^2$ of TiO$_2$ was retained on textiles, which equates to retention of 90% of TiO$_2$ between 10 and 40 cycles.

As discussed in Section 5.2, a large dislodgment of TiO$_2$ from PET textiles was observed after the first cycle of laundering, when PET was initiated with a concentration of 0.5 wt.%. The fibers acted as filters at the boundaries, where agglomeration of NPs initiated during the spraying of solution to the textile. On application of a high concentration, the filtering of NPs readily increased at these boundaries, and then formed larger agglomerates. As agglomeration increased, a film of NPs grew, as described by the schematic illustration in Figure 5.18(a). After hot-pressing by rigs, the agglomerates present at the boundaries of fibers presented a film on the surface. The film was a formation of loosely adhered and agglomerated NPs on the surface of fibers. The first cycle of laundering permitted a peeling of the NP film, which was easily dislodged, and thereby permitting the efficiently adhered and subsequent embedded NPs on the fiber surface, as described by the schematic illustration in Figure 5.18(b).
Sample PET/AT/C/0.25/0.7 had an initial measured content of TiO$_2$ of 20.3 µg/cm$^2$, with a deviation of ±2.2 µg/cm$^2$, on its surface before laundering, as presented in Figure 5.19. Greater than 80% of surface content was retained on the textile was noted after the first cycle of laundering, 16.8 µg/cm$^2$. The retention after 10 and 40 cycles was 13.6 and 12.7 µg/cm$^2$ of TiO$_2$ on textiles respectively. Removal of surface lying NPs by the first cycle, permitted retention of 76% of TiO$_2$ on sample PET/AT/C/0.25/0.7 between 1 and 40 cycles of laundering. This was regarded as a highly efficient textile for the adherence of NPs. A very low deviation from the mean existed after 40 cycles, ±0.7 µg/cm$^2$. A related t-test was applied for
the difference between data points of sample PET/AT/C/0.25/0.7 replicates, and yielded statistically insignificant results as \( P > 0.05 \). Hence, the null hypothesis that a difference existed between data points of sample PET/AT/C/0.25/0.7 replicates was rejected.

The increasing adherence of NPs on sample PET/AT/C/0.25/0.7 was attributed to the reduced agglomeration present at the fiber boundaries, and increasing efficiency of distribution of NPs on the textile surface, as presented by the schematic illustration in Figure 5.19(a). The finely distributed NPs permitted increased embedding into the fibers, which was due to the individual positioning of NPs on the fibers. The first laundering cycle dislodged the loosely adhered NPs, with minimal effect to the quality of distribution of NPs on the textile surface area, as described by the schematic illustration in Figure 5.19(b). The dislodged agglomerates had no effect on neighbouring NPs, as a film of NPs was not permitted and there existed no direct contact with neighbouring NPs. The removal of small agglomerates presented minimal risk of microbial colonisation due to the close proximity of neighbouring NPs, as illustrated by the distance separating neighbouring NPs in Figure 5.19(c). This efficient distribution of NPs best utilises the SA/V of NPs.
Figure 5.19 Results of TiO₂ (µg/cm²) versus cycles of laundering employing the automatic embedding techniques, with a 3 m/s textile transfer velocity, and a τ value of 0.7 was initialised with PET textiles and an applied concentration of 0.25 wt.% of TiO₂. A schematic illustration displaying a plan view of finely dispersed NPs over the textile surface, with minimal presence of agglomeration at the fiber boundaries (a), plan view of fibers displaying the removal of small agglomerates after the first laundering cycle (b), and efficient Distribution of NPs on sample PET/AT/C/0.25/0.7 (c).
Sample PET/AT/C/0.15/0.7 had an initial measured content of TiO$_2$ of 17.2 µg/cm$^2$ before laundering, as presented in Figure 5.20. After the first cycle of laundering, 15.2 µg/cm$^2$ was retained, which was greater than 80% of retention of TiO$_2$ on textiles. This was similar retention of NPs that sample PET/AT/C/0.25/0.7 had, but with a reduced content of TiO$_2$ on the surface. 90% of NPs were retained between the first and tenth cycle of laundering, where 12.6 µg/cm$^2$ was retained. Finally after 40 cycles, 10.1 µg/cm$^2$ was retained on textiles. Sample PET/AT/C/0.15/0.7 had 66% of NPs between 1 and 40 cycles of laundering retained.

This permitted a reduction durability of NPs compared to sample PET/AT/C/0.25/0.7, where sample PET/AT/C/0.15/0.7 also had a reduced content of TiO$_2$ after 40 cycles of laundering.

![Figure 5.20 Results of TiO$_2$ versus cycles of laundering employing automatic embedding techniques, with a 3 m/s textile transfer velocity, and a τ value of 0.7 was initialised with PET textiles and an applied concentration of 0.15 wt.% of TiO$_2$.](image)

Sample PET/AT/C/0.1/0.7 had 14 µg/cm$^2$ of TiO$_2$ present before laundering and a deviation ±1.6 µg/cm$^2$. After the first cycle, 11.5 µg/cm$^2$ was retained on textiles. Here 80% of the initial TiO$_2$ was efficiently embedded during the hot-pressing process. After 10 cycles, 9 µg/cm$^2$ was retained, permitting retention of 75% between 1 and 10 cycles of laundering. Finally 7 µg/cm$^2$ was permitted after 40 cycles, where 61% of TiO$_2$ was retained between 1 and 40 cycles of laundering.
Sample PET/AT/C/0.1/0.7 had the lowest retention and surface content of TiO$_2$ after 40 cycles of laundering for all values of the applied concentration of TiO$_2$.

![Graph showing TiO$_2$ versus laundering cycles](image)

Figure 5.21 Results of TiO$_2$ versus cycles of laundering employing automatic embedding techniques, with a 3 m/s textile transfer velocity, and a $\tau$ value of 0.7 was initialised with PET textiles and an applied concentration of 0.06 wt.% of TiO$_2$.

5.3.3. **Embedding of Acrylic and CA textiles by Automatic Rigs fitted with a Cotton Calender Roller**

The adherence and distribution of TiO$_2$-NPs was achieved on CA and acrylic textiles for their respective $\tau$ values, by automatic rigs fitted with a cotton calendar roller. The cotton calendar roller was fitted based on the outcomes of Section 5.3.2. The content of TiO$_2$ on textiles was quantified by analytical methods of AAS techniques, where 3 replicates of textile were analysed at cycles of 0, 1, 10 and 40 cycles of laundering. The applied concentration of TiO$_2$ to CA and acrylic textiles was set at a value of 0.25 wt.%, which was initiated from outcomes expressed in Section 5.3.2. The maximum value of $\tau$ for CA and acrylic textiles was quantified from the outcomes discussed in Section 4.1. The effective value of $\tau$ on CA and acrylic textiles was presented in Figure 5.22 and Figure 5.23.
CA textiles were prepared by automatic rigs employing values of 0.9 and 0.8 for $\tau$. The blue and red data points represent samples CA/AT/C/0.25/0.9 and CA/AT/C/0.25/0.8 respectively. The effects of varying $\tau$ values on the adherence of NPs to CA textiles were presented in Figure 5.22. Samples CA/AT/C/0.25/0.9 and CA/AT/C/0.25/0.8 permitted an initial content of 27.5 ±2 µg/cm² of TiO$_2$ before laundering. Sample CA/AT/C/0.25/0.9 had retained 19 µg/cm² after the first cycle of laundering, and 18 µg/cm² after 10 cycles. It was noted that the loosely adhered NPs were dislodged from CA textiles after the first cycle of laundering, where efficiently adhered NPs remained, and were then resistant to dislodgment even after 10 cycles of laundering. A lower value of $\tau$ permitted the reduced retention of TiO$_2$ on CA textiles after 10 cycles, 14 µg/cm². This was less than 50% of the initial TiO$_2$ that was applied. Samples CA/AT/C/0.25/0.9 and CA/AT/C/0.25/0.8 had severely reduced content of TiO$_2$ after 40 cycles of laundering, 6.4 ±0.8 and 4 ±0.5 µg/cm², which equates to 20% and 13% of TiO$_2$ respectively. The reduced retention may be an outcome of the concentration applied, where the optimised concentration of TiO$_2$ applied to CA textiles for efficient distribution should be pre-determined.

Figure 5.22 Results of TiO$_2$ versus cycles of laundering employing automatic embedding techniques, with a 3 m/s textile transfer velocity, and a $\tau$ value of 0.9 and 0.8, was initialised with CA textiles and an applied concentration of 0.25 wt.% of TiO$_2$. 

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Acrylic textiles were prepared by automatic rigs employing values of 0.7 and 0.6 for τ. The effective data collated for τ value on the adherence of NPs to acrylic textiles were presented in Figure 5.23. The blue and red data points represent samples ACR/AT/C/0.25/0.7 and ACR/AT/C/0.25/0.6 respectively. Sample ACR/AT/C/0.25/0.7 had an initial content of TiO\textsubscript{2} of 58 ±5 µg/cm\textsuperscript{2} before laundering. This content was substantially increased when a reduced value of τ was initiated for sample ACR/AT/C/0.25/0.6, where 92 ±9.7 µg/cm\textsuperscript{2} was permitted on acrylic textiles. There was an excessive deviation between specimens of sample ACR/AT/C/0.25/0.6. It was noted during preparation of acrylic textiles by automatic rigs, that sample ACR/AT/C/0.25/0.6 was increasingly wet after hot-pressing. The increasing wetness of sample ACR/AT/C/0.25/0.6 was a clear result of the reduced value of τ used, as there was minimal presence of wetness after hot-pressing of sample ACR/AT/C/0.25/0.7. Therefore, the increasing wetness permitted a 60% increase of content of TiO\textsubscript{2} on the acrylic textile.

After the first cycle of laundering, sample ACR/AT/C/0.25/0.7 retained almost 90% of TiO\textsubscript{2}, 50.3 ±5.1 µg/cm\textsuperscript{2}. This was further reduced to 34 µg/cm\textsuperscript{2} after 10 cycles of laundering. A final content of TiO\textsubscript{2} of 28 ±1.9 µg/cm\textsuperscript{2} was permitted after 40 cycles of laundering, which was over 50% of the initial permitted TiO\textsubscript{2} on textiles after embedding by automatic rigs, and retention of 60% between 1 and 40 cycles of laundering. Sample ACR/AT/C/0.25/0.6 had a significant reduction of content of TiO\textsubscript{2} after the first cycle of laundering, 45% which permitted retention of 63.4 ±9.2 µg/cm\textsuperscript{2}. It was noted that an excessive deviation remained between specimens analysed. Sample ACR/AT/C/0.25/0.6 had over 90% retention of TiO\textsubscript{2} between 1 and 10 cycles of laundering, where the deviation between specimens was finally reduced. Sample ACR/AT/C/0.25/0.6 retained 19.1 ±4.1 µg/cm\textsuperscript{2} of TiO\textsubscript{2} after 40 cycles, permitting retention of 20% between 0 and 40 cycles of laundering. The reduced τ value during hot-pressing by automatic rigs was considered the principle parameter in the reduction of TiO\textsubscript{2} on sample ACR/AT/C/0.25/0.6.
Figure 5.23 Results of TiO$_2$ versus cycles of laundering employing automatic embedding techniques, with a 3 m/s textile transfer velocity, and a $\tau$ value of 0.7 and 0.6, was initialised with acrylic textiles and a concentration of 0.25 (wt.%) of TiO$_2$ applied.

5.3.4. Summary

The technique of embedding NPs to textile surfaces requires a consistent approach through automatic application. Surface characterisation by imaging of PET textiles prepared with TiO$_2$, yielded efficient SA/V of NPS and consistent distribution where the applied concentration was lower than 0.5 wt.%. Textiles prepared by automatic rigs with a stainless steel calendar roller have low retention of NPs after cycles of laundering. The roller rapidly dissipated heat from the textile during pinching with the hot-press. This significantly reduced the temperature available for the elastic modulus of the PET to be reduced for sufficient embedding of NPs.

Changing the calendar roller from stainless steel to cotton permitted the thermal stability of the hot-press process during embedding of NPs. The outcomes correlated with data from techniques incorporating manual and semi-automatic embedding rigs, where an increasing value of $\tau$ permitted the increasing adhesion and durability of TiO$_2$-NPs to PET textiles. This was a factor of the reduced elastic
modulus of the PET initiated by the increasing temperature. The efficient distribution of NPs was a critical parameter in the prevention of microbial colonisation, as seen by data presented in ‘Appendix A’. The individual distribution of NPs permitted the efficient SA/V distribution of NPs, where NPs sufficiently prevented microbial colonisation in areas that were exposed by dislodgment of neighbouring NPs. Increasing the applied concentration yielded large agglomeration and formation of a film at the fiber boundaries. Large agglomerates were more readily dislodged, when loosely adhered to the textile surface. The increasing size of agglomerate permitted increasing abrasive contact during laundering. The optimum parameters permitting efficient embedding of TiO₂-NPs on PET textiles were set at a concentration of 0.25 wt.%, initiating a textile transfer velocity of 3 mm/sec and a τ value of 0.7.

The automatic embedding rig fitted with a cotton calender roller was efficiently employed with CA and acrylic textiles for the adherence of TiO₂-NPs to surfaces. A textile transfer velocity of 3 mm/sec was initiated with an applied concentration of 0.25 wt.% of TiO₂. An optimised value of τ was initiated with CA and acrylic textiles where an increasing value of τ permitted increasing efficiency of durability and adherence of NPs to surfaces. CA textiles permitted sufficient retention of TiO₂ after 10 cycles of laundering where a significant reduction of TiO₂ after 40 cycles existed. It was noted that a reduced value of τ permitted a significant wetness and content of TiO₂ after the embedding process. The increasing content coincided with a significant reduction of retention of TiO₂ after 40 cycles of laundering.

5.4. Conclusions
Manual, semi-automatic and automatic embedding rigs were successfully designed, developed and initiated to present conclusive outcomes of increasing the adherence and the distribution of NPs by embedding to the softened thermoplastic textiles. A manual embedding technique permitted the adherence of TiO₂-NPs to PET textiles, where an inefficient distribution of NPs over the textile surface was present. The manual application of TiO₂ solution and clamping of the hot-iron were factors that limited the control of distribution and embedding, distribution of TiO₂-NPs and
optimisation of the manual rig. A semi-automatic embedding rig was utilised to distribute a fine dispersion of NPs to the textile surfaces by a manually operated spray-gun and control of the temperature of textiles by a modified hot-press. Sporadic areas of high agglomeration were visibly present on PET textile surfaces, especially on the non-embedding side of the textile, which was noted as a consequence of the manual operated spray employed. The hot-press was limited by its maximum operating temperature, thereby inhibiting the optimum specification of embedding temperature for textiles by hot-pressing.

An automatic embedding rig supplied a continuous feed rate of textile under a fixed spray-nozzle that increasing the control of distribution and dispersion of NPs to textile surfaces. The applied concentration of NPs was the significant factor for optimising the distribution and dispersion of NPs on the textiles. The hot-plate supplied a controlled temperature to the textile surface, also permitting an optimum active temperature of hot-pressing for textiles. The control of temperature to the textile surface during the hot-pressing step was enhanced by replacing a steel calendar roller with a cotton calendar roller. Here the thermal conductivity of the roller was reduced, therefore preventing the heat loss between the hot-plate and the roller, and permitting the temperature of the textile to initiate a sufficient softening of the surface for embedding. A continuous textile surface embedded with NPs was successfully fabricated by automatic embedding rigs.

Surface characterisation by imaging using the SEM technique was successfully achieved to qualitatively assess the distribution of TiO$_2$-NPs on PET textile surfaces. The images highlighted the requirement of a controlled concentration during the application step of TiO$_2$ to the textile surface. An increasing applied concentration initiated a film of agglomerates of TiO$_2$ on the textile surface, where the NPs clustered and the film originated at the fiber boundaries. A reduction of the applied concentration permitted the distribution of a fine dispersion of NPs on the fiber surfaces, where the SA/V of NPs was efficiently utilised.
A method of quantifying the coverage of NPs on PET textiles was investigated by mapping using EDS techniques, where the technique proved unreliable for conclusive outcomes due to insignificant results. The inherent roughness of the textile surface, created by the warp and weft pattern of fibres, permitted a charging effect that was created by the secondary electrons bombarded on the surface by the EDS during mapping [75, 199], thereby reducing the precision of quantitative data by the mapping technique. The mapping of textiles permitted another method of qualitatively characterising textile surfaces embedded with NPs by visual characterisation.

The force required to *Pull-Off* a NP from a thermoplastic textile was investigated using a modified standard of ASTM D5451-09. A dollie was adhered to a textile surface by *adhesive-tape*, and the opposite end of the dollie was attached to an automatic adhesion tester, was then removed from the textile surface by a known force. There was no significant difference in the force required to remove the adhered dollie from a PET textile, and a PET textile with a coating of TiO$_2$ on its surface. An indirect method of quantifying the adherence of NPs was investigated, where replicates of *Pull-Off* testing were applied, and the resulting *adhesive-tapes* analysed by analytical techniques for the quantity of content of TiO$_2$ on surfaces. The outcomes highlighted insufficient quantities of TiO$_2$ present on the *adhesive-tapes* and a significant outcome could not be determined.

A laundering test using a standardised laundering machine for the laundering of textiles was successfully applied to define the durability of TiO$_2$-NPs to PET, CA and acrylic textiles. Textiles were successfully laundered up to 40 cycles, where the Ti present on a surface area of textile was quantified using analytical techniques by AAS.

PET textiles were coated and adhered with TiO$_2$-NPs by embedding rigs, where varying values of the normalised active temperature, $\tau$ and concentration, $\Omega$ of TiO$_2$ applied, were employed. As $\tau$ increased in value towards 1, the retention of TiO$_2$ to PET increased. The maximum value of $\tau$ permitted for PET textiles before plastic deformation was 0.7. Where a cotton calendar roller was employed with a textile transfer velocity of 3 m/s, and the concentration of TiO$_2$ applied was 0.25
wt.%, an optimum value of 0.7 for $\tau$ was determined. At this $\tau$ value, an initial content of TiO$_2$ of 20 $\mu$g/cm$^2$ was present. After 1 and 40 cycles of laundering, PET retained 17 $\mu$g/cm$^2$ and 13 $\mu$g/cm$^2$ of TiO$_2$, respectively.

The durability of NPs to PET textiles was optimum for efficient retention after 40 cycles of laundering, at an applied concentration of 0.25 wt.% of TiO$_2$ solution, and a $\tau$ value of 0.7. An increasing concentration of TiO$_2$ permitted large agglomerate sizes on PET textiles. Such agglomerates initiated formation of a thin film of NPs at the fiber boundaries, therefore permitting the dislodgment of NPs and the subsequent exposure of fiber surfaces by a peeling of the film. It was noted that increasing sizes of agglomerates initiated the increasing dislodgment of NPs from the textile surface, where large agglomerates were increasingly exposed to abrasion during laundering. The increase of abrasion may be a result of water or air flowing over and through the textile surface and pores, therefore penetrating the fiber boundaries and dislodging the agglomerates of NPs from the surface during laundering.

CA and acrylic thermoplastic textiles were successfully embedded with TiO$_2$-NPs by automatic rigs, and retention of NPs quantified by durability methods incorporating 40 cycles of laundering. A concentration of 0.25 wt.% of TiO$_2$ was applied to the textiles, permitting the future efficiency of retention by the optimisation of the applied concentration. Retention of NPs on CA and acrylic textiles significantly reduced after 40 cycles of laundering. CA and acrylic textiles had increasing retention of TiO$_2$ on their surfaces where a $\tau$ value of 0.7 and 0.6 was employed, respectively. The successful embedding of CA and acrylic with TiO$_2$-NPs confirmed the applicability of the automatic embedding technique to a variation of thermoplastic textiles, where the textiles permitted significant retention of TiO$_2$ on surfaces after 10 cycles of laundering.
6. Nanoparticle Embedding to Thermoplastic Textiles: Empirical Model

A suitable empirical model, approach and methodology, utilising the available data and focusing on the incidence of Retention of NPs to textile surfaces had been developed from the outcomes presented in Section 5.3.2. A simple non-linear regression model and forecast permitting the prediction of retention of TiO\textsubscript{2} on PET textiles after cycles of laundering can be employed with a high confidence. The adherence of NPs to textiles was examined by methods described in Section 3.4, where up to 40 cycles of laundering was considered. The parameters of applied concentration of TiO\textsubscript{2} and temperature setting of \( \tau \) permitted by the automatic embedding technique were considered. The outcomes confirm the applicability of this method for the data, and present a high prediction path for Retention of NPs to textiles after cycles of laundering. The empirical model describes the relationship between a multidimensional input, \( x \), and an output, \( y \). If \( x \) is a continuous variable, the task is termed a regression task and the model is known as a regression model. In this study, the input, \( x \) is a factor of cycles of laundering, \( N \) and the output, \( y \) is a factor of TiO\textsubscript{2}, by percentage (\%) or content (\( \mu g/cm^2 \)) retained on the textile surface.

The effect of the \( \tau \) value during hot-pressing was examined, where experimental and empirical data are analysed for efficiency of retention of NPs, collated from data in Section 5.3.2.1. Employing an optimum \( \tau \) value, the effect of applied concentration of TiO\textsubscript{2} (wt.\%) by spraying was assessed for adherence to PET textiles. An empirical equation was derived from data presented in Figure 5.18 to Figure 5.21, for retention of TiO\textsubscript{2} (\( \mu g/cm^2 \)) on PET textiles after varying cycles of laundering. Applying this equation, empirical values for TiO\textsubscript{2} (\( \mu g/cm^2 \)) content are assessed with experimental data, Figure 6.4 to Figure 6.7.

A standard measure of linear regression was applied for correlation between experimental and predicted curve relationships. The coefficient of determination, \( R^2 \) is a linear regression relationship between experimental and predicted curves [210]. It is a real number and independent of the units of
measurement, where absolute values vary between 0 and 1. When a linear relationship exists and each variable was perfectly predicted by the other, values increase to 1. When no linear relationship was present, the values reduce to zero [209]. This was calculated employing Eq.6-1:

$$R^2 = \frac{RSS}{TSS}$$

(6-1)

Where $RSS$ is the regression sum of squares of residuals, and $TSS$ is the total sum of squares.

6.1. Effect of Active Temperature on the Adherence of TiO$_2$-NPs to PET Textiles

This section presents a prediction model of an empirical relationship between retention of TiO$_2$ (%) after cyclic laundering of PET textiles, using varying values of $\tau$ during hot-pressing by automatic techniques, and data collated in Section 5.3. As discussed in Section 5.3, the first cycle of laundering was incorporated into the automatic embedding process, where surface lying and loosely adhered NPs were dislodged from the textile surface. The first cycle of laundering was considered a final step of the automatic embedding process. Retention of TiO$_2$ on the surface of PET after the first cycle of laundering was considered as the new baseline. The prediction of TiO$_2$ (%) that was efficiently adhered to PET textiles was investigated using the new baseline.

Figure 6.1 presents the retention of TiO$_2$ (%) on PET textiles for values of $\tau$, after 10 and 40 cycles of laundering, $N$. A line was predicted through a variable selection procedure, and identification of a 2$^{\text{nd}}$ order polynomial relationship was derived. Polynomial relationships are flexible and popular when no other theory is available. They are frequently employed when the response of data is curvilinear [209]. The 2$^{\text{nd}}$ order polynomial line derived in this study was of low order, two and therefore reducing over-fit of the data points [231]. A high order polynomial would have permitted the reduction of sensitivity and the ability to generalise new data points, thereby producing larger prediction errors. The coefficients of the polynomial assessed the position, width and orientation of the curve [209].
A least sum of squares was employed in the derivation of a 2\textsuperscript{nd} order polynomial equation for retention of TiO\textsubscript{2} (%) on PET after both 10 and 40 cycles of laundering, as presented in Figure 6.1 [209, 210]. The red data points highlight experimental data after 10 cycles of laundering. The continuous black line is a 2\textsuperscript{nd} order polynomial fit of the experimental data after 10 cycles. The blue data points highlight experimental data after 40 cycles of laundering, and the dashed black line is a 2\textsuperscript{nd} order polynomial fit of this experimental data. The slope indicates a parabolic relationship, where an increasing $\tau$ permits an increase of retention of TiO\textsubscript{2} (%). Retention of TiO\textsubscript{2} (%) on PET after 10 cycles of laundering was greater than on PET after 40 cycles. The slope at 40 cycles of laundering had a larger incline, therefore predicting an increase of retention for increasing values of $\tau$. A 10% difference of retention between 10 and 40 cycles of laundering existed at low values of $\tau$, and where values of $\tau$ was high the difference was 5%. This indicated an increasing compliance of PET surfaces to the embedding of NPs, with increasing values of $\tau$.

![Figure 6.1 Retention (%) of TiO\textsubscript{2} on PET textiles after 10 and 40 cycles of laundering, where experimental data were presented as red and blue data points after 10 and 40 cycles respectively. A 2\textsuperscript{nd} order polynomial relationship between experimental data points were presented in the form of a continuous, and dashed black line for 10 and 40 cycles of laundering respectively.](image-url)
Table 2.1 presents validation of the statistical fit of a 2nd order polynomial relationship to the experimental data for retention of TiO$_2$ (%) after 10 and 40 cycles of laundering. A related t-test was used to examine whether a significant difference existed between the experimental data and the derived 2nd order polynomial relationship of retention of TiO$_2$ (%) to PET, where parameters of $\tau$ are initiated. This yielded statistically insignificant results as viewed by $P > 0.05$. Hence, no difference between the experimental data and the 2nd order polynomial regression lines was apparent. The coefficient of determination, $R^2$ was the linear regression relationship between the experimental data and the polynomial fit [210]. An $R^2$ value close to 1 indicated a reliable regression fit.

### Table 6.1 The correlation coefficients of TiO$_2$ (%) retention on PET textiles with values of $\tau$, for experimental versus empirical data significance.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>$R^2$</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.967</td>
<td>1</td>
</tr>
<tr>
<td>40</td>
<td>0.976</td>
<td>1</td>
</tr>
</tbody>
</table>

Significance level ($P$ value) was 0.05

A 2nd order polynomial equation was derived for retention of TiO$_2$ (%) to PET after 10 cycles of laundering. The retention of TiO$_2$ (%) was predicted from Eq. 6-2:

\[
\%\text{ Retention} = 44.77\tau^2 - 11.30\tau + 65.80 \tag{6-2}
\]

Where the value of $\tau$ was assessed from Eq.4-1:

\[
\tau = \frac{\alpha}{\beta}
\]

And, $\alpha$, and $\beta$ from Eq. 4-2:

\[
\alpha = T_a - T_g
\]

And Eq.4-3:

\[
\beta = T_m - T_g
\]

This equation was used to predict the retention of TiO$_2$ (%) on a PET textile surface by inputting for independent variables of values of $\tau$. A maximum and a minimum retention of TiO$_2$ on surfaces were predicted by substituting in the limits for $\tau$. As $T_a$ was the only active variable, boundary conditions for the maximum retention of TiO$_2$ was calculated by substituting in for a maximum $T_a$, into Eq. 4-2. If the maximum value of $T_a$ was $T_m$, then:
\[ T_a = T_m \rightarrow \tau = 1 \]

The maximum retention of TiO\(_2\) on PET was quantified for a 0 value of \(\tau\). This gives retention of 99\% after 10 cycles of laundering. The maximum retention of TiO\(_2\) holds true for an ideal system. However, as discussed in Section 4.2, when experimental conditions were applied for \(\tau > 0.7\), the PET plastically strained beyond the elastic limit due to the reduction of its elastic modulus at elevated temperatures, as discussed in Section 4.2. The PET elongated and broke at the pinch point between the hot-plate and calender roller. Therefore, a maximum retention of TiO\(_2\) on PET after 10 cycles was 79\%, where a \(\tau\) value was optimised to 0.7. Boundary conditions for the minimum retention of TiO\(_2\) after 10 cycles were quantified by substituting for a minimum \(T_a\) into Eq. 4-2. If the minimum value of \(T_a\) was \(T_g\), then:

\[ T_a = T_g \rightarrow \tau = 0 \]

A minimum retention of TiO\(_2\) on PET was predicted for a 0 value of \(\tau\). This value permitted 66\% retention of TiO\(_2\) after 10 cycles of laundering.

A 2\(^{nd}\) order polynomial equation was derived for TiO\(_2\) (%) retention to PET after 40 cycles of laundering. The percentage retention of TiO\(_2\) was examined from Eq. 6-3:

\[
\text{% Retention} = 44.92\tau^2 - 3.79\tau + 55.13 \quad (6-3)
\]

Boundary conditions for a maximum retention of TiO\(_2\) after 40 cycles of laundering were assessed by substituting for a maximum \(T_a\), into Eq.4-2. If the maximum value of \(T_a\) was \(T_m\), then:

\[ T_a = T_m \rightarrow \tau = 1 \]

The maximum retention of TiO\(_2\) predicted on PET was recorded as 96\% after 40 cycles of laundering. As previously discussed, the maximum retention of TiO\(_2\) was through for an ideal system where no strain was applied to the textile. Using the automatic embedding process, a maximum setting of 0.7 for a value \(\tau\) was employed. Therefore, the maximum retention of TiO\(_2\) achieved on PET after 40 cycles of laundering was 74\% for a 0.7 value of \(\tau\). Boundary conditions for the minimum retention of TiO\(_2\) after 40 cycles were predicted by substituting for a minimum \(T_a\), into Eq. 4-2. If a minimum value of \(T_a\) was \(T_g\), then:

\[ T_a = T_g \rightarrow \tau = 0 \]

The minimum retention of TiO\(_2\) permitted on PET textiles after 40 cycles was 55\%.
The retention of TiO₂ (%) was high for a 0 value of τ. These prediction models require correlation with data values of TiO₂ (µg/cm²) from Section 5.3. The content of TiO₂ (µg/cm²) on PET at zero cycles of laundering using a 0.1 value for τ, presented 15.1 ±1.9 (µg/cm²) of TiO₂ on the PET surfaces. In contrast to this, the content of TiO₂ on PET at zero cycles of laundering using a 0.7 value for τ permitted 20.5 ±2.3 (µg/cm²) of TiO₂. Therefore, the PET textiles prepared with a reduced value of τ, permitted a reduction of content of TiO₂ (µg/cm²) surfaces after automatic embedding, as presented in the results of Section 5.3.2.1. The effective reduction of content of TiO₂ (µg/cm²) on PET textiles employing a reduced value of τ, has been discussed in Section 5.3.

6.1.1. Summary

An empirical model was derived for the prediction of retention of TiO₂ (%) permitted on PET for values of τ after 10 and 40 cycles of laundering. The data points were collated from Section 5.3, where embedding of TiO₂-NPs on PET textiles employing the automatic technique using a cotton calender roller was achieved. The theory fitted a 2nd order polynomial relationship, where a good statistical fit was permitted (P > 0.05). The increasing retention of TiO₂ (%) permitted on PET increasing with values of τ. The retention of TiO₂ (%) was a percentage of the content of TiO₂ (µg/cm²) on PET, where this content varied with values of τ. The prediction line should be used in conjunction with the values of content when making a prediction of percentage retention of TiO₂ to textiles after 10 and 40 cycles of laundering. A reduction of values of τ permitted a reduction of content on PET after hot-pressing with automatic rigs.

The retention of TiO₂ (%) on PET textiles was examined after 10 cycles of laundering, for values of τ by Eq.6-2:

\[ \% \text{Retention} = 44.77\tau^2 - 11.30\tau + 65.80 \]

The maximum value of τ cannot be greater than 0.7, as a temperature beyond this value will plastically deform the PET thermoplastic textile. Therefore the maximum percentage retention of TiO₂ permitted on PET after 10 cycles of laundering using a
The retention of TiO$_2$ (%) on PET textiles was quantified after 40 cycles of laundering, for values of $\tau$ by Eq.6-3:

$$\%\text{ Retention} = 44.92\tau^2 - 3.79\tau + 55.13$$

As already discussed, the maximum value of $\tau$ cannot be greater than 0.7, as the increasing temperature beyond this value will plastically deform the PET textile. The maximum percentage retention of TiO$_2$ achieved on PET after 40 cycles of laundering using a $\tau$ value of 0.7, was 74%. The percentage retention of TiO$_2$ using a $\tau$ value of 0 was 55%.

### 6.2. Effect of the Applied Concentration on the Adherence of TiO$_2$-NPs to PET Textiles

In this section, an empirical relationship was assessed for the content of TiO$_2$ ($\mu$g/cm$^2$) retained after cyclic loading by laundering of PET textiles that were prepared with values of applied concentration, $\Omega$ of TiO$_2$ (wt.%). This relationship was designed by examining the experimental data presented in Section 5.3. Retention of TiO$_2$ ($\mu$g/cm$^2$) permitted on PET was assessed for cycles of laundering, $N$ between values of 0 to 40, and an applied concentration of 0.5, 0.25, 0.15, 0.06 (wt.%) of TiO$_2$. The outcomes fitted a log-normal relationship for the data collated in Section 5.3.2.2.

A prediction equation was formulated by employing a variable selection procedure, and the identification of a log-normal distribution was derived for the curve profile. A line was drawn on the foundation of Eq.6-4:

$$TiO_2 = \Delta ln\ N + \lambda$$

In this line, the content of TiO$_2$ ($\mu$g/cm$^2$) on PET textiles was the dependent variable, and cycles of laundering, $N$ were the independent variable, where $\Delta$ and $\lambda$ are coefficients of the line. The observed outcome of content of TiO$_2$ ($\mu$g/cm$^2$) existed in the interval $[0,\infty]$. 

$\tau$ value of 0.7, was 79%. The percentage retention of TiO$_2$ using a $\tau$ value of 0 was 66%.
A goodness of fit between the experimental data and log-normal relationships was supplied in Table 6.2. $R^2$ values close to 1 permitted a reliable regression fit. A related t-test was employed to examine if a significant difference existed between experimental and log-normal relationships of TiO$_2$ ($\mu g/cm^2$) on PET at cycles of $N$. This yielded statistically insignificant results as viewed by $P > 0.05$. Hence, no difference between the experimental and log-normal regression lines was present. As $\Delta$ was negative, the increase in cycles of laundering permitted a decreasing content of TiO$_2$ ($\mu g/cm^2$) on PET. Where $\Delta$ was not sufficiently large, content of TiO$_2$ ($\mu g/cm^2$) was not proportional to $N$ [209].

<table>
<thead>
<tr>
<th>Concentration (wt.%)</th>
<th>$\Delta$</th>
<th>$\lambda$</th>
<th>$R^2$</th>
<th>Sig (P Value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-3.2</td>
<td>21.1</td>
<td>0.9246</td>
<td>1</td>
</tr>
<tr>
<td>0.25</td>
<td>-1.3</td>
<td>17.0</td>
<td>0.9384</td>
<td>0.068</td>
</tr>
<tr>
<td>0.15</td>
<td>-1.2</td>
<td>14.9</td>
<td>0.9788</td>
<td>0.273</td>
</tr>
<tr>
<td>0.06</td>
<td>-1.1</td>
<td>11.5</td>
<td>0.9929</td>
<td>0.273</td>
</tr>
</tbody>
</table>

The significance level ($P$ value) was 0.05

The data points of $\Delta$ and $\lambda$ listed in Table 6.2, were plotted against concentrations of 0.5, 0.25, 0.15 and 0.06 (wt.%) of TiO$_2$. A line was formulated by a variable selection procedure, and identification of a 2nd order polynomial relationship was derived. The blue data points represent the data of $\Delta$ and $\lambda$ presented in Figure 6.2 and Figure 6.3, respectively, and the black line represents a 2nd order polynomial fit. The polynomial expression relates to the variables $\Delta$ and $\lambda$. Where the independent variable of cycles of laundering, $\Omega$ was raised to successive integer powers beyond the first integer, the equation was nonlinear [210]. The slope presented in Figure 6.2 permitted a parabolic relationship, where the increasing applied concentration (wt.%) decreased the values of $\Delta$. As the coefficient $\Omega^2$ was negative, this implies an inverted parabola. A line was drawn on the foundation of Eq.6-5, where $\Delta$ was given as:

$$\Delta = -14.82\Omega^2 + 3.6\Omega - 1.3$$

(6-5)

$\Omega$ represents the applied concentration of TiO$_2$ (wt.%) that was sprayed on the PET. The applied concentration, $\Omega$ must be greater than zero to satisfy Eq.6-5.
The 2\textsuperscript{nd} order relationship presented a single inflection point, where the relationship changed. This initiated at an applied concentration of 0.12 wt.% of TiO\textsubscript{2}, as highlighted in Figure 6.2. The negative squared term in Eq.6-5 permitted an inverted parabola relationship.

Figure 6.2 Plot of \(\Delta\) versus applied concentration of TiO\textsubscript{2} (wt.%). An inverted 2\textsuperscript{nd} order polynomial relationship was presented.

The profile also implied a parabolic relationship, where increasing the applied concentration permitted an increasing value of \(\lambda\), as presented in Figure 6.3. As the coefficient of \(\Omega^2\) was negative, the parabola of Eq.6-5 was therefore inverted. A line was drawn on the foundation of Eq.6-6, where \(\lambda\) was determined as:

\[
\lambda = -32.34 \Omega^2 + 39.7\Omega + 9.33
\tag{6-6}
\]

Where, \(\Omega\) was the applied concentration of TiO\textsubscript{2} (wt.%). The concentration, \(\Omega\) must be greater than zero for Eq.6-6 to exist. The 2\textsuperscript{nd} order relationship permitted a single inflection point, where the relationship changed. This transpires when the concentration reaches 0.61 wt.\%, as highlighted in Figure 6.3. This was a linear regression line, as the relationship involved an independent variable in the form of cyclic loading, \(N\) [209]. The term linear was employed as, \(\Omega^2\) and, \(\Omega\) are unknown linear parameters of the linear function, Eq.6-6.
Figure 6.3 Plot of λ values versus applied concentration of TiO₂ (wt.%). A 2nd order polynomial relationship was presented.

There was a sufficient quantity of data points in Figure 6.2 and Figure 6.3 to formulate a significant relationship between the respective data. Increasing the data points between the concentrations of 0.25 and 0.5 wt.% of TiO₂ would be impractical, as outcomes from Section 5.2 and 5.3 have presented the lack of durability and dispersion of NPs in this region of applied concentration of TiO₂. In the case that more data points were required, the assessment should be initiated where the applied concentration was between 0.25 and 0.06 wt.% of TiO₂.

A goodness of fit between the 2nd order polynomial relationship and the data plots of Δ and λ were presented by black lines in Figure 6.2 and Figure 6.3 respectively, and the data values are listed in Table 6.3. The regression fits were calculated by applying the regression sum of squares of residuals, RSS as a function of the total sum of squares, TSS [209]. $R^2$ values increasing to 1 indicated a reliable regression fit. A related t-test assessed whether a significant difference existed between experimental and logarithmic relationships of Δ and λ coefficients at parameters of applied concentration of TiO₂ (wt.%). This yielded statistically insignificant results as viewed by $P > 0.05$. Hence, no difference between the coefficients and 2nd order polynomial regression lines was observed.
<table>
<thead>
<tr>
<th>Slope</th>
<th>$R^2$</th>
<th>Sig (P Value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$</td>
<td>0.9978</td>
<td>0.715</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.9971</td>
<td>1</td>
</tr>
</tbody>
</table>

The significance level (P value) was 0.05

A regression model for the prediction of content of TiO$_2$ on PET textiles was derived by substituting Eqs.6-5 and 6-6 into Eq.6-4, where the dependent variable was content of TiO$_2$ ($\mu$g/cm$^2$), and the independent variables were the applied concentration of TiO$_2$ (wt.%), $\Omega$ and cycles of laundering, $N$. This permitted the derivation of Eq.6-7:

$$TiO_2 = (-14.8 \Omega^2 + 3.6\Omega - 1.3) \ln N + (-32.3\Omega^2 + 39.7\Omega + 9.3) \quad (6-7)$$

Eq.6-7 was applied to predict content of TiO$_2$ ($\mu$g/cm$^2$) on PET textiles after 0, 1, 10 and 40 cycles of laundering, where the applied concentrations that was sprayed on the textiles were 0.5, 0.25, 0.15 and 0.06 (wt.%) of TiO$_2$. Experimental data were plotted with the empirical data, as presented in Figure 6.4 to Figure 6.7. The blue data points represented the experimental data values, and the black line represented the curve estimation by empirical data, predicted by employing Eq.6-7, where a good statistical fit was permitted with experimental data as $P > 0.05$.

![Figure 6.4 Results of TiO$_2$ ($\mu$g/cm$^2$) versus cycles of laundering, N by automatic embedding techniques, where a 3 m/s textile transfer velocity was employed, a $\tau$ value of 0.7 was initialised with PET textiles, and employing a concentration of 0.5 wt.% of TiO$_2$.](image)
Figure 6.5 Results of TiO$_2$ (µg/cm$^2$) versus cycles of laundering, $N$ by automatic embedding techniques, where a 3 m/s textile transfer velocity was employed, a $\tau$ value of 0.7 was initialised with PET textiles, and employing a concentration of 0.25 wt.% of TiO$_2$.

Figure 6.6 Results of TiO$_2$ (µg/cm$^2$) versus cycles of laundering, $N$ by automatic embedding techniques, where a 3 m/s textile transfer velocity was employed, a $\tau$ value of 0.7 was initialised with PET textiles, and employing a concentration of 0.15 wt.% of TiO$_2$. 
A goodness of fit, \( R^2 \), between the empirical relationship predicted by employing Eq.6-7, and the experimental data were supplied in Table 6.4. These were examined by applying a regression sum of squares of residuals, \( RSS \) as a function of the total sum of squares, \( TSS \) [209]. \( R^2 \) values close to 1 indicated that a reliable regression fit existed. A related t-test was employed to assess if a significant difference existed between the experimental and empirical relationships of content of \( \text{TiO}_2 \) (µg/cm\(^2\)) permitted on PET after cycles of laundering, \( N \). The test yielded statistically insignificant results, as viewed by \( P > 0.05 \). Hence, no difference existed between the experimental and empirical results.

Table 6.4 Correlation coefficients for the prediction of \( \text{TiO}_2 \) (µg/cm\(^2\)) content on PET textiles, employing concentrations of 0.5, 0.25, 0.15 and 0.06 \( \text{TiO}_2 \) (wt.%). The linear regression and significance (Sig) between experimental and empirical results were presented.

\[
\begin{array}{|c|c|c|}
\hline
\text{Concentration (wt.\%)} & \text{\( R^2 \)} & \text{Sig (P Value)} \\
\hline
0.5 & 0.924 & 1 \\
0.25 & 0.981 & 0.273 \\
0.15 & 0.986 & 0.285 \\
0.06 & 0.991 & 0.273 \\
\hline
\end{array}
\]

The significance level (\( P \) value) was 0.05
6.2.1. Summary

An empirical model was derived for the prediction of retention of TiO$_2$ (µg/cm$^2$) permitted on PET thermoplastic textiles for values of concentration of TiO$_2$ (wt.%) at varying cycles of laundering, $N$. The data was collated from Section 5.3, where embedding of TiO$_2$-NPs to PET textiles by automatic hot-pressing techniques with a cotton calender roller was achieved. The data fitted a log-normal distribution, and Eq.6-4 was derived with good significance ($P > 0.05$). The coefficients, $\Delta$ and $\lambda$ from Eq.6-4, were plotted against the applied concentration of TiO$_2$ (wt.%), and a curve profile was modelled by the derivation of a 2$^{nd}$ order polynomial relationship, thereby permitting Eq.6-5 and Eq.6-6. Substituting Eqs.6-5 and 6-6 into Eq.6-4, a model presenting the surface content of TiO$_2$ (µg/cm$^2$) on PET after cycles of laundering, $N$ for any concentration of TiO$_2$ (wt.%) applied during the automatic embedding process was predicted by Eq.6-7, where a good statistical fit was permitted with experimental data ($P > 0.05$).

$$\text{TiO}_2 = (-14.8\Omega^2 + 3.6\Omega - 1.3) \ln N + (-32.3\Omega^2 + 39.7\Omega + 9.3)$$

The model presented a method of predicting the retention of TiO$_2$ after laundering of textiles, and displayed the effectiveness of distributing NPs on a textile by a finely dispersed spray. An increase of the applied concentration permitted an initial high content of TiO$_2$ (µg/cm$^2$) on the PET, presenting inefficient use of the applied TiO$_2$. A reduction of the applied concentration to an optimum quantity permitted a lower initial content of TiO$_2$, although this enabled greater efficiency of durability of the TiO$_2$ that was initially present on the surface after spraying.

6.3. Conclusions

Empirical models were derived for the prediction of retention of NPs to thermoplastic textiles, where TiO$_2$-NPs were embedded to PET textiles by the automatic embedding rig. The effect of the normalised active temperature, $\tau$ on the retention of TiO$_2$ to PET was successfully modelled and correlated with a high degree to the experimental data ($P > 0.05$). In this empirical model the initial laundering cycle was incorporated as a step in the automatic embedding technique,
where the step removed NPs that were lying on the surface and were not embedded into the surface. The TiO$_2$-NPs that were retained after the initial laundering cycle were used as the benchmark. Incorporating data from PET textiles prepared with a concentration of 0.25 wt.% of TiO$_2$, and varying values of $\tau$, the percentage of retention of TiO$_2$ after 40 cycles of laundering was plotted against values of $\tau$, where a 2$^{nd}$ order polynomial curve was predicted. The curve estimation permitted the prediction of percentage retention of TiO$_2$ to PET with high significance ($P > 0.05$). The retention by percentage can be predicted by the empirical model after 10 and 40 cycles of laundering for values of $\tau$. Increasing TiO$_2$ retention to PET was present with increasing values of $\tau$, while the maximum $\tau$ cannot be greater than a value of 0.7, as beyond this value the PET textile plastically deforms, and was unrecoverable.

The effect of concentration of TiO$_2$ (wt.%) applied to PET textiles was derived to present an empirical model for content of TiO$_2$ ($\mu$g/cm$^2$) on PET textiles. A model was successfully derived with high confidence, permitting the prediction of retention after cycles of laundering, $N$ and applied concentration, $\Omega$ of TiO$_2$. Experimental data collated from durability testing of PET prepared by automatic rigs using varying concentrations of TiO$_2$ were analysed for curve estimations, predicting a log-normal curve for concentration. Plotting constants of the log-normal curves permitted a curve estimation of a 2$^{nd}$ order polynomial. An empirical model was derived, permitting a prediction of content of TiO$_2$ ($\mu$g/cm$^2$) on PET, where concentration of TiO$_2$ (mg/l) and cycles of laundering, $N$ are the inputs. TiO$_2$ ($\mu$g/cm$^2$) content can be predicted with high significance and correlated with a high degree to the experimental data ($P > 0.05$).
7. Conclusions and Future Work

This chapter presents a summary of the conclusions derived from the detailed experimental and theoretical work carried out in Chapters 4-6 and draws general conclusions. It also answers the research questions set out in Section 1.2 and then tests the Hypothesis outlined in Section 1.3. The chapter then proposes a few directions in which future work can be carried out for the embedding of NPs to thermoplastic textiles.

7.1. Theoretical Considerations in Relation to the Embedding of NPs in Thermoplastic Textiles

The enhanced compliance of thermoplastic textiles was initiated when the textile was heated above the glass transition temperature, $T_g$ permitting embedding of NPs with a still lower applied load. The heating of the thermoplastic textile is associated with a reduction of the modulus of elasticity of the textile. Dynamic mechanical testing of a thermoplastic textile at elevated temperatures presented a reduction of elastic response by the application of an applied load, and therefore decreasing the load required for plastic deformation of a PET textile at temperatures lower than its melting temperature, $T_m$. This permitted a reduction of the force required for embedding NPs, increased the contact radius and the subsequent displacement of the NPs into the fiber surface.

These outcomes along with the known mechanical and physical properties of PET and NPs of TiO$_2$ were applied to two variants of contact mechanics: the JKR model and the DMT model, (Section 4.4). The study has found that embedding of NPs was better described by the JKR model [223] due to its higher sensitivity to the reduction of the stiffness, the size of the NP and the type of textile. Reducing the elastic response of PET textiles permitted an increasing contact radius of NP on its surface for a lower applied load. The NPs were embedded with a force that overcame the elastic limit of the textile, therefore plastically deforming the surface of the fiber at the point where the NPs were in contact, and embedding them into the surface. This
micromechanical understanding was critical in optimising experimental parameters to obtain the best durability of embedding of NPs in textiles.

7.2. Embedding NPs to Single-Side of the Thermoplastic Textiles
Incorporating the outcomes of theoretical considerations, a methodological approach to experimentally embed NPs into thermoplastic textiles was examined. Manual, semi-automatic and automatic embedding rigs were successfully designed, constructed and employed to control the distribution and to increase the adherence of NPs by embedding in the surface-softened thermoplastic textiles (Section 3.2). The manual embedding technique permitted adherence of NPs of TiO$_2$ to PET textile surfaces, where an inefficient distribution of NPs over the textile surface was present, as viewed by imaging techniques. A semi-automatic embedding rig was utilised to distribute a fine dispersion of NPs to the textile surfaces by applying NPs using a spray-gun, and control of heating of textiles by a modified hot-press. An automatic rig supplied a continuous feed rate of textile under a fixed spray-nozzle that enhanced the control and efficiency of distribution and dispersion of NPs on textile surfaces.

The concentration of NPs that were applied by spraying was the significant factor for optimising distribution and dispersion on textiles. Increasing the applied concentration to textiles presented agglomeration of TiO$_2$ as a film at the fiber boundaries. An optimum concentration permitted a fine homogeneous dispersion of NPs over the textile surface. The hot-plate supplied a controlled temperature to the surface, and also permitted an optimum active temperature of hot-pressing for textiles using a cotton calender roller with low thermal conductivity and minimal heat loss to the textile surface. A continuous textile surface embedded with NPs was successfully produced by automatic embedding rigs.

Quantification of the distribution of NPs and the strength of adherence required specially designed methodology. For example, an EDS mapping of textile surfaces provided quantitative data of Ti present. These data however need to be considered with caution as no significant differences were found in the EDS concentration of Ti between textiles that were sprayed with two significantly different
starting concentrations (0.25 wt.% and 0.15 wt.%). Perhaps the instrument sensitivity was too low to perform such analysis with confidence. More surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS) and/or Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) may resolve this issue.

The force required to *Pull-Off* a NP from a thermoplastic textile was investigated using a modified standard of *ASTM D5451-09*. An indirect method of quantifying the adherence of NPs was investigated, where replicates of *Pull-Off* testing were applied, presenting insufficient quantities of Ti on the *adhesive-tapes* for a conclusive outcome.

A laundering process using a standardised laundering machine was successfully applied to textiles, where durability of NPs to PET, CA and acrylic textiles surfaces was tested. As the active temperature of the hot-press increases in value, the retention of TiO$_2$ to textiles increased. Increasing the applied concentration of TiO$_2$ permitted larger agglomerate sizes that produced a formation of agglomerate films. Large agglomerates permitted the increasing dislodgment of NPs from the textile surface, where they were exposed to abrasion during testing of their durability to textiles.

CA and acrylic thermoplastic textiles were successfully embedded with NPs of TiO$_2$ by automatic embedding rigs, and proving the applicability of the embedding technique by hot-pressing for multiple types of thermoplastic textile variations. The textiles retained NPs after 10 cycles of laundering, where retention was low after 40 cycles of laundering.

The best parameter for durability of NPs to PET textiles was found to be: at an applied concentration of 0.25 wt.% of TiO$_2$, and a normalised active temperature for a 0.7 value of $\tau$ using a textile feed rate of 3 mm/sec, and a spray-nozzle supplying 0.05 l/min.
7.3. The Durability of NPs embedded in Thermoplastic Textiles: An Empirical Model

Empirical models were successfully derived to predict the retention of NPs to thermoplastic textiles as a function of active temperature of embedding and the cycle of laundering. The effect of the normalised active temperature, $\tau$ on the retention of TiO$_2$ to PET textiles was successfully modelled and correlated with a high degree to the experimental data (Section 6.1). Curve estimation allowed for the prediction of retention of TiO$_2$ (%) to PET textiles with high significance ($P > 0.05$). Increasing retention of TiO$_2$ to PET was present with increasing values of $\tau$.

The effect of applied concentration of TiO$_2$ (wt.%) to PET textiles was successfully derived with high confidence to present an empirical model for TiO$_2$ ($\mu$g/cm$^2$) content on PET textiles after laundering (Section 6.2). The model permitted a prediction of TiO$_2$ ($\mu$g/cm$^2$) content on PET fabric, where concentration of TiO$_2$ (mg/l) and cycles of laundering, $N$ are the inputs. TiO$_2$ ($\mu$g/cm$^2$) content can be predicted with high significance and correlated with a high degree to the experimental data ($P > 0.05$).

7.4. Answers to the Research Questions and Testing the Research Hypotheses

The study, in particular helped us to find answers to the following research questions:

1. Will a reduced elastic modulus of thermoplastic textiles during embedding of NPs improve their adherence to the textile?

The study has found that reduction of the elastic modulus during embedding of NPs significantly help both to reduce the applied force of embedding and increases the adherence of the NPs as seen in the durability test (Section 5.3.2.). It has been reported in this study that thermal increase of the thermoplastic textiles coincided with the activation of the thermal transitions (Section 4.1). These transitions initiated varying degrees of textile softening by reducing the elastic modulus, as shown by dynamic testing using DMA (Section 4.2). Incorporating this data, theoretical considerations highlighted the
effect of reducing the elastic modulus of the surfaces when embedding NPs (Section 4.2 & 4.3). Here the lower elastic modulus permitted increased displacement of NPs into the textile surface for a lower applied load. Assessment of NP durability to textiles by experimental methods using laundering standards, presented outcomes where increasing retention of NPs was present on textiles with increasing temperature of the textile (Section 5.3.2.1). As increasing temperature of thermoplastic textiles was directly related to the reduction of elastic modulus, it can be said that the reduced modulus improves NP adherence to textiles.

2. What is the most suitable treatment to permit efficient adherence of NPs to single-side of a thermoplastic textile surface?

This study has found that a suitable treatment was achieved by applying an optimised concentration of NPs in a solution for a fine dispersion of NPs to single-side of the textile (Section 5.3). The treatment also incorporates applying a surface-softening heat to single-side of the textile, while clamping the textile and NPs to a non-embedding side that has a low thermal conductivity. The fine dispersion of NPs was critical to their efficient adherence on surfaces (Section 5.1-5.3). NPs required placement on single-side of the textile as small agglomerates or as individual particles, so that when a particle was dislodged the neighbouring particles were not affected or dislodged, and the resulting exposed surface area was not sufficient for microbial colonisation (Section 5.3.2). This was not the case for a coating or film of NPs present on the single-side of the textile surface, where peeling of the NP coating had initiated the exposure of a large area of fiber surface for the possibility of microbial attack (Section 5.1-5.3). The application of the surface softening heat to the NP sprayed side of the textile was the most suitable treatment for efficient adherence of NPs to textiles on single-side. A non-embedding side with high thermal conductivity permitted lower adherence of NPs to textiles (Section 5.3.1). This high thermal conductivity increased the time it took for the textile to reach a temperature that permitted sufficient softening of its surface, and therefore the efficient embedding of NPs into its
surface. The best treatment therefore involved applying a cotton calender roller of low thermal conductivity (Section 5.3.2).

3. Is it possible to embed NPs to thermoplastic textiles through softening of the textile surface by automatic rigs?

Automatic rigs have proved successful in the softening of thermoplastic textiles for the embedding of NPs into these surfaces (Section 5.3). The scaling of manual and semi-automatic rigs enabled design of the optimum operating parameters and the equipment in the design of automatic rigs (Section 3.2). The automatic rig produced a textile with a homogeneous distribution of finely dispersed NPs over single-side of its surface (Section 5.3). This technique automatically transferred the textile under a fixed spray-nozzle that coated the textile with an optimised concentration of TiO$_2$ solution, and then continuing the textile in between a hot-plate and a cotton calender roller, that both created the surface-softening and the pressure for sufficient embedding, respectively. The textile proved abrasive to durability testing (Section 5.3), and efficiently decomposed bacteria (Section A.2).

4. Will thermoplastic textiles prepared by embedding techniques with NPs have effective adherence during abrasive testing?

The adherence of NPs to textiles prepared by embedding techniques, have been assessed using methods of *Pull-Off* testing with significant outcomes not present (Section 5.2.3). However, abrasive testing by laundering of textiles has provided conclusive outcomes that prove the effective adherence of NPs to thermoplastic textiles using embedding techniques (Section 5.3). Using a standard process and machine for the laundering of textiles, the TiO$_2$ content remaining on textiles was quantified by AAS techniques, and empirical models were designed based on this data (Section 6.1 & 6.2). The outcomes highlighted that for the best prepared sample; almost 80% of TiO$_2$ remained on textiles between 1 and 40 cycles of laundering, which was considered very effective adherence of NPs on textiles during abrasive testing.
The current work was conducted on the foundation of three research hypotheses as outlined in Section 1.3. The research findings in Chapters 4, 5 and 6 can now be used to test these hypotheses as follows:

**Hypothesis 1: The softening of thermoplastic textiles can be exploited to obtain a textile coated on single-side by strongly adherent NPs.**

The softening of thermoplastic textiles was successfully exploited by heat addition, to coat single-side of its surface by embedding of commercially available NPs of TiO₂. This hypothesis was therefore true to the extent that when the softening temperature was at its optimum, the NPs were retained on a PET thermoplastic textile even after the textile was laundered. CA and acrylic thermoplastic textiles were also processed in a similar way, where the heat addition for softening of the textile surface was optimised for the particular textile. This highlights the applicability of embedding of NPs by softening the thermoplastic surface through heat addition, where a diverse range of thermoplastic textiles can be processed, and proves Hypothesis 1 as correct.

**Hypothesis 2: The extent and strength of binding of these NPs will be related to the degree of softening.**

The binding strength of NPs to thermoplastic textiles was related to the degree of softening by the application of a durability test using laundering as a method of testing the adherence of NPs. Durability testing successfully illustrated that increasing the temperature of thermoplastic textiles above the glass transition, $T_g$, achieved by the heat addition using embedding rigs, correlated with the enhanced durability of NPs to textile surfaces. An empirical model was derived to predict the extent and the strength of binding of NPs on textiles, where these models display the relationship between softening of textiles and durability of NPs to their surfaces.
**Hypothesis 3:** The distribution of NPs on the surface of the textile can be controlled by employing a coating process by spraying and varying its parameters.

The distribution of NPs was efficiently controlled by optimising the concentration of NPs applied to textile surfaces by a spray through a nozzle. An increasing homogeneity of the coating of NPs over the textile surface was successfully achieved by scaling up and automating a hot-pressing embedding technique: from manual; to semi-automatic; and finally automatic rigs. An optimum concentration of applied NPs for spraying was achieved for PET textiles.

### 7.5. Future Work

The future work planned by the author during the development of these textiles includes, but are not limited to:

1. Design of a model by analytical techniques for assessment of flight of NPs from a spray-nozzle, and the effective contact and embedding into textile surfaces on impact. This will permit an understanding of the force and energy required to embed a NP into a surface by spraying, and the optimisation of the distribution on the textile surface.

2. Development of a finite element analysis (FEA) model would present a method of modelling the embedding of NPs into thermoplastic textile surfaces. This model permits a greater understanding of contact mechanics theories, and the effective temperature on thermoplastic materials embedded with NPs. A measurement of the *Pull-Off* force required for NP dislodgment would also be assessed.

3. Incorporation of other NPs such as ZnO and Ag doped TiO$_2$, which have antibacterial abilities to be embedded into thermoplastic textiles by automatic embedding techniques. These NPs will broaden the scope of antibacterial abilities, and the products that can be developed promoting antibacterial action.

4. Incorporation of NPs into cellulosic fibers, such as cotton, by automatic embedding techniques. Cellulosic fibers are a common fiber used in the textiles
and clothing industry, especially in the area of comfort, therefore enabling a greater scope of technological applications of the automatic embedding technology.

5. Design of a bench style technique for the quantification of antimicrobial/antibacterial properties on textile surfaces, without the requirement of clinical strains. This will permit a cheaper and safer method of quantifying the content of NPs and durability to surfaces.

6. The use of surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS) and/or Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS). These techniques will permit a broader scope of textile surface characterisation and allow quantification of surface content and coverage.
8. References


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82. Colorists, A.A.o.T.C.a., *Colorfastness to Perspiration*, 2009, AATCC Committee RA50: North Carolina, USA.


A. Appendix

A.1 Antimicrobial Rigs for Testing of Textiles

The photocatalytic ability of PET textile surfaces incorporated with TiO$_2$-NPs were investigated against microbes of *MRSA*, *E. coli* and *C. albicans* for their survival ratio in standard lighting conditions, darkness and when irradiated by UVA light. Textiles were prepared by employing automatic embedding rigs, as discussed in Section 3.2.4. The ability of textiles to kill bacteria, the time of exposure, and the concentration of TiO$_2$ applied to textiles were the essential parameters assessed in the antimicrobial test.

The schematic presented in Figure A.1, illustrates the rig employed for antimicrobial activity of textiles against bacteria. The bacteria and the textiles were insulated in a glass container, for control of the experiment and health and safety purposes of the operator. The textiles were situated on a glass holder, with the non-embedded side of the textile facing down towards the cooling system. Bacteria were placed on the embedded side of the textile surface. The glass container was sealed with a quartz glass window. The textile sample was illuminated with an Ultraviolet-A light, which was positioned above the embedded side of the textile. The light was directly shone on the textiles, thereby permitting optimum exposure of UV-A.

![Figure A.1 Schematic illustration of antimicrobial test rig for microbial analysis of textiles.](image)

*Figure A.1 Schematic illustration of antimicrobial test rig for microbial analysis of textiles. Courtesy of Wrut. Reproduced from [10].*
Figure A.2 presents antimicrobial survival ratio of MRSA against PET textiles. Textiles were prepared by automatic embedding techniques applying concentrations of 1, 0.5, 0.25, 0.15 and 0.06 wt.% of TiO$_2$ to 100% PET textiles. Good killing of MRSA is present on textiles after 100 minutes of irradiation by UV-A light on all textiles. As irradiation time reduces, the kill rate of bacteria also reduces.

![Graph showing antimicrobial survival ratio of MRSA against PET textiles.](image)

**Figure A.2** Antimicrobial survival ratio of MRSA against PET textiles. Textiles were prepared by automatic embedding techniques applying concentrations of 1, 0.5, 0.25, 0.15 and 0.06 wt.% of TiO$_2$ to 100% PET textiles. Reproduced from [10]
Figure A.3 presents the reduction (%) of MRSA against laundering cycles ($N$). The textiles were laundered at intervals of 0, 1, 10 and 40 cycles. The graph presents microbial data of textiles at these intervals. The textile used was 100% PET as discussed in Section (3.1), by the automatic rigs discussed in (Section 3.2.4). The applied concentration was 0.15 wt.% of TiO$_2$. A value of 0.7 was used for $\tau$. Outcomes indicate efficient reduction of MRSA on PET textiles after the illumination time by UV-A. There still existed reduction in dark conditions. The PET has an inherent antimicrobial ability even when not coated by TiO$_2$.

![Graph showing antimicrobial reduction of MRSA against PET textiles](image)

Figure A.3 Antimicrobial reduction of MRSA against PET textiles. Textiles were prepared by automatic embedding techniques applying concentrations of 0.15 wt.% of TiO$_2$ to 100% PET textiles using 0.7 value for $\tau$. Reproduced from [10]
Figure A.4 presents the reduction (%) of *MRSA* against laundering cycles (*N*). The textiles were laundered at intervals of 0, 1, 10 and 40 cycles. The graph presents microbial data of textiles at these intervals. The textile used was 100% PET as discussed in Section (3.1), by the automatic rigs discussed in (Section 3.2.4). The applied concentration was 0.5 wt.% of TiO$_2$. A value of 0.7 was used for $\tau$. Outcomes indicate efficient reduction of *MRSA* on PET textiles after illumination time by UV-A. These outcomes indicate that no extra benefit from microbial activity was achieved by using higher applied concentrations of TiO$_2$. As outcomes from using a lower concentration of TiO$_2$, seen in Figure A.3 highlight good antimicrobial activity for a concentration of 0.15 wt.%.

**Figure A.4** Antimicrobial reduction of *MRSA* against PET textiles. Textiles were prepared by automatic embedding techniques using applied concentrations of 0.5 wt.% of TiO$_2$ to 100% PET textiles using 0.7 value for $\tau$. Reproduced from [10]
B. Appendix

Figure B.1 and Figure B.2 present a prototype design for the fully automatic embedding rig.

Figure B.1 Longitudinal view of fully-automatic embedding rig.

Figure B.2 3-D view of Fully automatic embedding rig.
C. Appendix

Figures C.1-C.6 present some of the outcomes of Ti (%) against Au (%) by EDS mapping on adhesive-tape samples discussed in Section 5.2.3.

Figure C.1 EDS characterisation of adhesive-tape from Figure 4.12(c), displaying confirmation of TiO\textsubscript{2} and percentage Ti on the surface compared to gold sputtering.

Figure C.2 EDS characterisation of adhesive-tape from Figure 4.12(d), displaying confirmation of TiO\textsubscript{2} and percentage Ti on the surface compared to gold sputtering.
Figure C.3 EDS characterisation of adhesive-tape from Figure 4.13(c), displaying confirmation of TiO$_2$ and percentage Ti on the surface compared to gold sputtering.

Figure C.4 EDS characterisation of adhesive-tape from Figure 4.13(d), displaying confirmation of TiO$_2$ and percentage Ti on the surface compared to gold sputtering.
Figure C.5 EDS characterisation of adhesive-tape from Figure 4.14(c), displaying confirmation of TiO$_2$ and percentage Ti on the surface compared to gold sputtering.

Figure C.6 EDS characterisation of adhesive-tape from Figure 4.14(d), displaying confirmation of TiO$_2$ and percentage Ti on the surface compared to gold sputtering.
D. Appendix

Conversion from Ti in mg/l of HF and H₂O solution to µg/cm² of TiO₂

AAS data output of 1 mg/l is equivalent to 1 ppm

Using an arbitrary value of 4 mg/l

Converting 4 mg to 1000 g

Where the HF and H₂O sample volume of 30 ml = 30 g

The mass of Ti in this solution is given as:

4 mg = 0.004 g

Therefore: 0.004 g – 1000 g

Where: Ti – 30 g

Gives:

\[ Ti = \frac{0.004 \times (30)}{1000} \rightarrow 0.00012 \ g \rightarrow 0.12 \ mg \]

If the textile sample size is (4 x 4 cm²)

Then: 0.12 mg – 16 cm²

And: x – 1 cm²

Gives:

\[ Ti = \frac{0.12 \times (1)}{16} \rightarrow 0.0075 \ mg/cm² \rightarrow 7.5 \ µg/cm² \]

If 4 ppm – 7.5 µg/cm²

And 1 ppm – Ti

Giving the quantity of Ti on a (4 x 4 cm²) textile sample using 30 ml of H₂O:

\[ Ti = \frac{1 \times (7.5)}{4} \rightarrow 1.875 \ µg/cm² \]

For conversion of Ti to TiO₂,

Where the molar mass of \( M_{Ti} = 47.9 \ g/mol \)

And \( M_O = 2.16 \ g/mol \)

Therefore:

\[ M_{TiO₂} = M_{Ti} + 2 \times M_{O} \rightarrow 47.9 + 2 \times 2.16 \]

Giving a TiO₂ content of 79.9 g/mol

According to stoichiometry the molar number:

\[ \eta_{Ti} = \eta_{TiO₂} \]
Using: 47.9 g – 1.875 µg/cm²

And: 79.9 g – TiO₂

\[
TiO₂ = \frac{1.875 \times (79.9)}{47.9} \rightarrow 3.128 \, \mu g/cm²
\]

Converting output values from AAS for Ti to TiO₂ gives:

1 ppm → 3.128 µg/cm²