Photocatalytic behaviour of nano sized titanium dioxide (TiO$_2$) blended in poly (lactic acid) (PLA) via melt blending method: focus on textile applications

Chengjiao Zhang
Description: Thesis submitted for the degree of Master in Science in Textile Engineering

Title: Photocatalytic behaviour of nano sized titanium dioxide (TiO₂) blended in poly (lactic acid) (PLA) via melt blending method: focus on textile applications

Author: Chengjiao Zhang

Supervisors: Anders Persson, Vincent Nierstrasz

Examiner: Anders Persson

The Swedish School of Textiles
Report No.: 2013.14.3
Abstract
During this project, photocatalytic material, nano sized titanium dioxide, was introduced into poly (lactic acid) to produce functional surface capable of self-cleaning property. Samples containing 0%, 5%, 10%, 15% and 20% titanium dioxide were prepared and etched with proteinase K to expose the nano particles on the surface.

It was shown that the nano titanium dioxide could dispersed in the polymer matrix pretty well, it was also found that the nano particles affected the thermal and mechanical properties of the polymer matrix differently, due to difference in concentrations of nano filler.

The self-cleaning property was evaluated by decolouration of stains caused by coffee and red wine, also by detecting degradation of methylene blue via a UV-vis spectrophotometer. By measuring changes in absorbance of light at 664nm wavelength after a maximum of 24h UV irradiation, it was possible to measure the degradation property of the samples.

During this project, it was found that titanium dioxide could be introduced into PLA via blending, and it was possible to etch the composite with enzyme. During the self-cleaning property test of stains, changes in colour were only observed on red wine stain, not for coffee stain. For methylene blue degradation, sample containing 15% titanium dioxide undergone 6 hours etching time gave the best degradation result, which totally degraded the methylene blue after irradiated under UV for 24 hours.

Key words: Titanium dioxide (P25), poly(lactic acid)(PLA), self-cleaning surface, photocatalyst, photocatalytic activity, enzymatic degradation, methylene blue photo-degradation.
Popular abstract

The concept of self-cleaning surface was firstly inspired by lotus leaf, dirt can hardly stick on its surface and could be easily removed by water. This is caused by its structure, the lotus leaf has a wax like surface which makes it extremely water repellent and in micro scale, the lotus leaf has a rough surface, which minimize the contact area between the dirt and the surface, making the dirt could be easily removed by water or rain. All of them together make the lotus leaves have self-cleaning property. Different with this concept, the self-cleaning property could also be caused by titanium dioxide due to its unique property. When exposed to UV or high energy light, titanium dioxide could decompose organic dirt into water and air, nano titanium dioxide now could be used in textile industry to produce textiles with self-cleaning property. Poly (lactic acid) (PLA) is polymer similar with polyester in some properties; it is derived from 100% renewable source like corn and has been broadly used in textile applications.

In this study, the mostly commercially used titanium dioxide powder was added into PLA to produce a product with self-cleaning surface. Films with different concentration of nano titanium dioxide were prepared. To make product has self-cleaning property, the surface PLA need to be removed to make the titanium dioxide expose on the surface. The self-cleaning behaviour of the product with was tested by different materials such as stains of coffee and red wine, if the product works, the stain colour will disappear after some time.
# Table of content

Abstract .................................................................................................................................1
Popular abstract ..................................................................................................................2
List of figures .......................................................................................................................4
List of tables .........................................................................................................................6
1. Introduction ......................................................................................................................7
   1.1 Aim of project ..............................................................................................................7
   1.2 Research questions .....................................................................................................8
   1.3 Delimitations of project ............................................................................................8
2. Literature review ..............................................................................................................9
   2.1 Self-cleaning textiles ..................................................................................................9
   2.2 Titanium dioxide (TiO$_2$) ......................................................................................9
   2.3 Properties of TiO$_2$ ..............................................................................................11
   2.4 Apply titanium dioxide in textile substrate ............................................................14
   2.5 Poly(lactic acid) (PLA) .........................................................................................19
   2.6 Poly(lactic acid) (PLA) degradation ......................................................................20
3. Material ..........................................................................................................................21
   3.1 PLA ..........................................................................................................................21
   3.2 Titanium dioxide ......................................................................................................21
   3.3 Enzyme ....................................................................................................................21
   3.4 Chemicals .................................................................................................................21
4. Method ............................................................................................................................22
   4.1 Sample production ....................................................................................................22
   4.2 Etching treatment .....................................................................................................23
   4.3 Characterisation .......................................................................................................25
5. Result ...............................................................................................................................28
   5.1 Sample production ....................................................................................................28
   5.2 Etching treatment .....................................................................................................29
   5.3 Characterisation .......................................................................................................32
6. Discussion and analysis .................................................................................................43
   6.1 Prototype production ...............................................................................................43
   6.2 Etching ......................................................................................................................44
   6.3 Surface characterisation .........................................................................................47
   6.4 Mechanical properties .............................................................................................48
   6.5 Thermal properties ..................................................................................................49
   6.6 Self-cleaning property evaluation ...........................................................................50
7. Conclusion .......................................................................................................................53
8. Further development .......................................................................................................53
Acknowledgement .............................................................................................................54
Reference ............................................................................................................................55
Appendix A: Enzymatic etching .........................................................................................65
Appendix B: Surface and cross section .......................................................... 67
Appendix C: Data of mechanical test ............................................................... 72
Appendix D: Data for DSC ........................................................................... 73
Appendix E: TGA ......................................................................................... 74
Appendix F: Decolouration of stains ............................................................... 76
Appendix G: Methylene blue degradation ...................................................... 78

List of figures

Fig.2.1 Schematic of the generation of highly oxidative radicals under UV light at the 
TiO$_2$ surface. ....................................................................................... 13
Fig.2.2: Mechanism of photocatalytic decompose of organic dirt. ............. 14
Fig.4.1 Schematic of prototype production ................................................. 23
Fig 4.2 Schematic of decolouration of stains, distance between UV and samples was 
20cm. .................................................................................................... 27
Fig.5.1 Rheology characterisation of raw materials: the test was carried out at 230°C, 
shear rate range was 0.01-100 l/s. Blue curve indicates PLA6201, red curve for 
PLA 3051, Green for PLA4042. ............................................................ 28
Fig.5.2 Cross section of pure PLA: a) before enzymatic degradation; b) after 6 h 
enzymatic degradation ........................................................................ 32
Fig.5.3 Surface of pure PLA film with about 500pixel in width, 1pixel =0.26mm; a) 
before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) 
after 6 h degradation. ............................................................................ 33
Fig.5.4 Surface of 20% TiO$_2$ with about 500pixel in width, 1px =0.26mm: a) before 
enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 
h degradation. ...................................................................................... 33
Fig.5.5 Cross section of 20% TiO$_2$: a) before enzymatic degradation; b) after 2 h 
degradation; c) after 4 h degradation; d) after 6 h degradation ............... 34
Fig.5.6 DSC result for samples before enzymatic etching .......................... 35
Fig.5.7 DSC Result of pure PLA samples before and after enzymatic etching.... 36
Fig.5.8 DSC Result of 20% TiO$_2$ samples before and after enzymatic etching .... 36
Fig.5.9 TGA result for samples before enzymatic etching ........................... 37
Fig.5.10 TGA Result of pure PLA samples before and after enzymatic etching .... 38
Fig.5.11 TGA Result of 20% TiO$_2$ samples before and after enzymatic etching ... 38
Fig.5.12 UV-vis absorption spectra of MB solution, for 5%TiO$_2$ samples with the 
highest weight loss after enzymatic treatment ........................................ 40
Fig.5.13 UV-vis absorption spectra of MB solution, for 10%TiO$_2$ samples with the 
highest weight loss after enzymatic treatment ........................................ 40
Fig.5.14 UV-vis absorption spectra of MB solution, for 15%TiO$_2$ samples with the 
highest weight loss after enzymatic treatment ........................................ 41
Fig. 5.15 UV-vis absorption spectra of MB solution, for 20% TiO$_2$ samples with the highest weight loss after enzymatic treatment.

Fig. 5.16 UV-vis absorption spectra of MB solution for 20% TiO$_2$ samples with the lowest weight loss after enzymatic treatment.

Fig. B.1 Surface of pure PLA film with about 500px in width, 1px = 0.26mm: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation.

Fig. B.2 Cross section of pure PLA: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation.

Fig. B.3 Surface of 5% TiO$_2$ with about 500px in width, 1px = 0.26mm: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation.

Fig. B.4 Cross section of 5% TiO$_2$: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation.

Fig. B.5 Surface of 10% TiO$_2$ with about 500px in width, 1px = 0.26mm: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation.

Fig. B.6 Cross section of 10% TiO$_2$: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation.

Fig. B.7 Surface of 15% TiO$_2$ with about 500px in width, 1px = 0.26mm: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation.

Fig. B.8 Cross section of 15% TiO$_2$: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation.

Fig. B.9 Surface of 20% TiO$_2$ with about 500px in width, 1px = 0.26mm: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation.

Fig. B.10 Cross section of 20% TiO$_2$: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation.

Fig. D.1 DSC Result of 5% TiO$_2$ samples before and after enzymatic etching.

Fig. D.2 DSC Result of 10% TiO$_2$ samples before and after enzymatic etching.

Fig. D.3 DSC Result of 15% TiO$_2$ samples before and after enzymatic etching.

Fig. E.1 TGA Result of 5% TiO$_2$ samples before and after enzymatic etching.

Fig. E.2 TGA Result of 10% TiO$_2$ samples before and after enzymatic etching.

Fig. E.3 TGA Result of 15% TiO$_2$ samples before and after enzymatic etching.

Fig. F.1 Samples with 5% TiO$_2$, the enzymatic etching time could be seen on the top of each picture: a, e, i) before UV irradiation; b, f, j) after 3 days irradiation; c, g, k) after 7 days irradiation; d, h, l) after 10 days irradiation.

Fig. F.2 Samples with 10% TiO$_2$, the enzymatic etching time could be seen on the top of each picture: a, e, i) before UV irradiation; b, f, j) after 3 days irradiation; c, g, k) after 7 days irradiation; d, h, l) after 10 days irradiation.
Fig. F.3 Samples with 15% TiO$_2$, the enzymatic etching time could be seen on the top of each picture: a, e, i) before UV irradiation; b, f, j) after 3 days irradiation; c, g, k) after 7 days irradiation; d, h, l) after 10 days irradiation. 77

Fig. F.4 Samples with 20% TiO$_2$, the enzymatic etching time could be seen on the top of each picture: a, e, i) before UV irradiation; b, f, j) after 3 days irradiation; c, g, k) after 7 days irradiation; d, h, l) after 10 days irradiation. 77

Fig. G.1 UV-vis absorption spectra of MB solution, for 5% TiO$_2$ samples with the lowest weight loss after enzymatic treatment. 78

Fig. G.2 UV-vis absorption spectra of MB solution, for 10% TiO$_2$ samples with the lowest weight loss after enzymatic treatment. 78

Fig. G.3 UV-vis absorption spectra of MB solution, for 5% TiO$_2$ samples with the lowest weight loss after enzymatic treatment. 79

List of tables

Table 2.1: summary of methods. 16
Table 5.1 Weight loss of pure PLA in alkaline solution at 37°C in slow shaking water bath, varying in alkaline concentration and processing time. 29
Table 5.2 Weight loss of pure PLA in 1.5M Tris-HCl buffered solution enzyme solution at 37°C in slow shaking water bath, varying in processing time. 30
Table 5.3 Weight loss of PLA containing 10wt% titanium dioxide in 30mM Tris-HCl buffered enzyme solution at 37°C in slow shaking water bath, varying in processing time. 30
Table 5.4 Weight loss of PLA containing 10 wt% titanium dioxide in 20mM phosphate buffered enzyme solution at 37°C in slow shaking water bath, varying in processing time. 30
Table 5.5 average weight loss of one piece of sample after enzymatic treatment, samples undergone 2 and 4 hours treatment shared the same solution, samples undergone 6 and 15 hours treatment shared the same solution. 31
Table 5.6 per unit weight loss of one piece of sample after enzymatic treatment, samples undergone 2 and 4 hours treatment shared the same solution, samples undergone 6 and 15 hours treatment shared the same solution. 32
Table 5.7 Result of tensile strength. 34
Table 5.8 Result of flexural test. 34
Table 5.9 Decolouration of coffee and red wine stains under UV irradiation. 39
Table 5.10 Changes in absorbance of MB solution during the photodegradation process. 42
Table A.1 Original data of enzymatic etching. 67
Table C.1 Original data of tensile strength. 72
Table C.2 Original data of flexural strength. 72
1. Introduction

Self-cleaning textiles have been widely investigated and two categories of methods could have been used to produce textiles with self-cleaning property. The traditional strategy used to get textiles with self-cleaning property was to make the textiles have extremely hydrophobic surface, which aimed to increase the contact angle between the surface and contaminant. Using this approach, it is very difficult for the contaminant to stay in the textile surface and very easy to remove. However, the drawbacks of this strategy make it necessary to find an alternative. The most important disadvantage of this strategy is the environmental issue. So far, it is still impossible to produce super hydrophobic textiles without fluoride carbons, which are harmful to environment and human beings. (Malik T. et al., 2013)

The other new emerged strategy, with the development of nano technology, used to get self-cleaning fabrics is to apply photocatalytic materials on the textile substrate. By utilizing the photoreaction induced by photocatalytic material, when the textile substrate expose to certain irradiations, irradiations with higher energy than the band gap of the photocatalytic material, the organic contaminants will be degraded into air and water on the photocatalytic material surface. (Malik T. et al., 2013)

Titanium dioxide gets a lot attention during past decades and is taken as one of the most promising photocatalytic materials that could be used in textile industry for many advantages such as low band gap, UV protection. (HASHIMOTO K. et al., 2005)

There are different phases of titanium dioxide existing, in crystalline phase or amorphous phase. But not all the phases could be found in the nature and not all phases of titanium dioxide have the photocatalytic activity. In general, only titanium dioxide in rutile or anatase phase has photocatalytic activity. (HASHIMOTO K. et al., 2005)

In order to apply nano sized titanium dioxide on textile substrate, both functional coating and melt blending approaches could be used. The functional coating method has been investigated by a lot of researchers. However, it is still not easy to get a good adhesion between the inorganic nano particle and the textile substrate. Meanwhile, less investigation has been carried out on the melt blending method. (Senič Ž. et al., 2011)

1.1 Aim of project

The aim of this thesis is to investigate the possibility to create a self-cleaning surface based on nano photocatalytic titanium dioxide and poly (lactic acid) (PLA) via melt blending method and how the composite will perform self-cleaning property under UV irradiation after enzymatic etching. Besides that, the self-cleaning surface should
be applicable for textile applications.

1.2 Research questions

- Is it possible to combine nano titanium dioxide with poly (lactic acid) polymer via melt blending method?
  - How the nano filler will influence the property polymer resin?

- Is it possible to etch the composite with enzyme to make the nano filler expose on the surface?
  - How the etching will affect the property of the composite?

- How the final samples perform self-cleaning property?
  - The relation between the concentration of titanium dioxide and the self-cleaning property?
  - How will enzymatic etching influence the self-cleaning function?

1.3 Delimitations of project

The raw PLA materials used in this project are limited to the three grades available in the school. During the etching treatment, the result is based on the specimens described in chapter 4, different result might be obtained for sample with different shape or different prepare method. Pictures for surface characterization was taken by the digital microscopy with a constant parameters, brightness may differs if parameter changes. During the function evaluation, all samples were irradiated by the same UV light with a wave length of 365nm.
2. Literature review

2.1 Self-cleaning textiles

The self-cleaning textiles indicate textiles with a surface that can clean itself without laundering action. Self-cleaning surface could be generally classified into two categories-hydrophobic and hydrophilic. The former concept was first inspired by the lotus effect, dirt can hardly stick on lotus leaves and could be easily removed by droplet or rinse of water. The lotus effect is basically obtained by the structure of the leaf. The lotus leaf has a waxy like surface that makes it extremely water repellent and together with rough surface in micro scale, makes the lotus leaf has a self-cleaning property. By mimicking the nature, textiles with self-cleaning property could be manufactured. (Malik T. et al., 2013)

Fluorocarbons, carbon compound contains fluorinated carbon chains, are essential to produce hydrophobic self-cleaning textiles, by using fluorocarbons, products with very low surface tension and extremely high water contact angle could be obtained. Textiles manufactured by this method are not only repellent to water, but also odour, coffee and red wine stains. On the other hand, the effect will decrease after laundry and the fluorocarbons are harmful to environment and human beings. (Malik T. et al., 2013)

The hydrophilic self-cleaning method, commonly refers to the photocatalytic effect, is usually known as introducing a photocatalyst, such as titanium dioxide, on a substrate surface to induce photoreaction on its surface. By utilizing the catalytic self-cleaning process, the surface attached dirt could be chemically decomposed by oxidation reactions with the presence of specific lights. (Walid D., 2008)

2.2 Titanium dioxide (TiO₂)

Titanium dioxide, also called titanium (IV) oxide or titania, was discovered in 1821 and commercialized in the early 20th century. (Chaharmahali A. R., 2012) Since its discovery, titanium dioxide has been widely used as white pigment since ancient time and now the annual consumption was above 4.4 million tons in 2006. (Feng L., 2006) There are at least 8 different crystalline structures of titanium dioxide, four naturally polymorphs (rutile, anatase, bookite, TiO₂ (B)) and four high press laboratory synthesized (TiO₂ (II), TiO₂ (H), baddelleyite and cotinnite). (Chaharmahali A. R., 2012) Among them, anatase, rutile and bookite are the most common crystalline forms and most manufactured worldwide. However, most researches have been focused on the photocatalytically active of anatase and rutile. There is no test has been done on the photocatalytic activity of bookite (Senić Ž. et al., 2011).

According to Dastjerdi and Montazer (2010), anatase is metastable at lower temperatures and is most applicable in catalysis and photo-catalysis because of its
higher surface area. The anatase form of titanium dioxide is more efficient in photocatalytic activity than rutile. The rutile is more thermodynamically stable than the anatase and brookite. At high temperature, anatase and brookite are converted into rutile and rutile is the most important source for white pigment in industry. (Zhang H. and Banfield J. F., 1998)

2.2.1 Synthesis of TiO₂ nanoparticles

Since the discovery of TiO₂, different methods have been developed to synthesize TiO₂ nanoparticles, some of them being: sol-gel, sol, micelle and inverse micelle methods, hydrothermal method, solvothermal method, direct oxidation method, chemical and physical vapor depositions, electrodeposition, sonochemical method and microwave method. For most of them, high temperatures are usually necessary to get high crystalline TiO₂ nanoparticles. (Chen X. and Mao S., 2007) However, when taken into consideration into the applications of TiO₂ on textile substrate, the synthesis methods at low temperature with high TiO₂ crystalline nanoparticles are most appreciated as most textile substrate could not withstand high temperatures. From that viewpoint, among all the methods, sol-gel and hydrothermal methods could are more appreciated in textile industry. (Senić Ž. et al., 2011)

In textile industry, the sol-gel synthesis seems like the most promising method for the TiO₂ nanoparticles preparation since it has some unique advantages: low temperature, versatility of performance and homogeneity of product at molecular level. (Senić Ž. et al., 2011) In a typical sol-gel process, a sol, or a colloidal suspension, is formed via a hydrolysis and polymerization reaction of TiO₂ precursors. The precursors are usually inorganic metal salts such as titanium sulfate (Ti(SO₄)₂) (Zhang H. et al, 2012), ammonium fluotitanate ((NH₄)₂TiF₆)(Qu J. et al, 2010) and titanium (IV)chloride (TiCl₄) (Mihailovic D. et al, 2011), or metal organic compounds such as titanium tetraisopropoxide(TTIP) (Tung W.S. and Daoud W.A., 2008) and (Uddin M. J. et al, 2007). During the reaction, the process started with a hydrolysis of TiO₂ precursor catalyzed by acid into titanium (IV) alkoxide (Ti(OH)₄), then condensation and polymerization reaction followed that leads to the formation of Ti–O–Ti chains, the principle is shown in scheme 1:

≡Ti-OR + H₂O → ≡Ti-OH + ROH - Hydrolysis
≡Ti-OH + HO-Ti≡ → ≡Ti-O-Ti≡ + H₂O - condensation
≡Ti-OH + RO-Ti≡→≡Ti-O-Ti≡ + ROH - polymerization

Scheme1. Sol-gel synthesis of TiO₂ nanoparticles

Those reactions lead to a liquid sol phase, complete polymerization and loss of solvent lead to the conversion from the liquid into a gel phase. (Chen X. and Mao S., 2007)
2.2.2 Applications

Currently, besides acting as the most important source of white pigment, because of the unique optical, photocatalytic, electric and hydrophilic properties, TiO$_2$ nano-particles have gained extensive attention as an attractive multifunctional material for remarkable applications in many fields. The existing and promising applications of TiO$_2$ nanomaterials include paint, toothpaste, UV protection, photocatalysis, sensing, electrochromics and photochromics. The electronic band gaps of titanium dioxides are 3.02eV for rutile and 3.2eV for anatase, which is almost equivalent to a wavelength of UV light and result in high absorption of UV light region. Besides that, TiO$_2$ nanoparticles are stable, non-toxic, all of them allow them to be applied for UV protection purposes. (Dastjerdi R. and Montazer M., 2010).

The most attractive and promising property of TiO$_2$ is the photocatalytic activity. TiO$_2$ is now regarded as the most efficient and environmental friendly photocatalysis and has been widely used for antibacterial and photodegradation applications. (Chen X. and Mao S., 2007) According to HASHIMOTO K. et al (2005), scientific studies on such photoactivity of TiO$_2$ have been reported since the early part of the 20th. According to the research of Feng L. (2006), a major landmark of TiO$_2$ used as photocatalyst was the discovery by Fujishima and Honda in 1972, during that year, they discovered that TiO$_2$ could be used as catalytic electrode in photoelectrolysis cell to decompose water into H$_2$ and O$_2$, without the application of a voltage. Since then, much attention has been given to apply TiO$_2$ to degrade organic compounds such as virus, bacterial and other organic contaminants. (Feng L., 2006)

In addition to applications above, TiO$_2$ also has been widely used to induce super hydrophilic property (SAWADA K. et al, 2003); use as carrier of noble metal such as silver to get more efficient photocatalytic activity (Dastjerdi R. and Montazer M., 2010, 2011); reversible redox mediators; TiO$_2$ electrodes; solar cell and gas sensor, which is dependent upon changes in its electrical conductivity upon gas adsorption like SnO$_2$ and ZnO semiconductors (Feng L., 2006).

2.3 Properties of TiO$_2$

In the work of Chen X. and Mao S. (2007), they expounded that both anatase and rutile can be described in terms of chains of TiO$_6$ octahedra, where each Ti$^{4+}$ ion is surrounded by an octahedron formed by six O$^{2-}$ ions. The two crystals are different in the distortion of the octahedron and the pattern of the octahedral chains. In anatase, its symmetry is lower than orthorhombic because the octahedron of anatase is significantly distorted while for rutile, the octahedron shows a slight orthorhombic distortion. The Ti-Ti distance of rutile is shorter than that of anatase, whereas the Ti-O distance of rutile is larger than those of anatase. In rutile structure, each octahedron is connecting with 10 neighbor octahedrons, two of them share edge oxygen pairs and the other eight share corner oxygen atoms. Meanwhile, in anatase structure, each octahedron connects
with eight neighbors, four of them share an edge and four share a corner. These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO$_2$.

Zhang H. and Banfield J.F.(1998) investigated the phase stability of the rutile and anatase using a thermodynamic analysis. In their research, they found that anatase becomes more stable than rutile when the particle size decreases below 14 nm. This result also has been proven by other researchers, according to Chen X. (2009), he described in his work that for bulk material, rutile is more stable than anatase and bookite at high temperature, but the particle size in nanoscale, anatase and bookite have the same stability. On heating contaminant with coarsening, anatase and bookite will transformed into rutile.

TiO$_2$ has a very complex surface and the surface is extremely sensitive to thermo chemical history such as impurity, temperature, pressure. Principally, the surface contains several atoms, ions and molecules by ionic, covalent or coordinated bonding such as basic terminal and acidic bridged hydroxyl groups. TiO$_2$ surface are capable of absorbing, dissociating or reacting with a wide range of inorganic and organic molecules under certain conditions. (Feng L.,2006) The most important of them is the water adsorption, even the fact has been given a lot attention and many research have been done regarding this issue, but there is still no unanimous detailed agreement on the nature of adsorption.( Diebold U., 2003)

### 2.3.1 Photocatalytic activity

One of the most important properties that make TiO$_2$ as attractive material is the photocatalysis property. In chemistry, photocatalysis is defined as the acceleration of a photoreaction in the presence of a catalyst, during the reaction, TiO$_2$ will accelerate or induce photoreaction without affecting itself. Many applications of TiO$_2$, including applications in textile field, are focus on utilizing this property to get product with self-cleaning and antibacterial functions. (Yuranova T. et al, 2007)

It has been proven that among the three natural crystalline forms of TiO$_2$-anatase, rutile and bookite, anatase and rutile crystal are photo catalytically active while bookite has never been tested. As a photocatalyst, pure anatase is more effective than pure rutile, however, the best catalytic activity is obtained by a mixture of anatase and rutile, for example, Degussa P25,which is the most affective commercially used and has been proven having higher photo catalytic activity, mixing of about 80% anatase and 20% rutile. (Yuranova T. et al, 2007)

The mechanism of photoreaction induced by TiO$_2$ was extensively studied and explained by many researchers, some of them are Dastjerdi R. and Montazer M.(2010), Senič Ž. et al. (2011), Yuranova T. et al (2007) and Chen X. and Mao S.(2007), when
TiO$_2$ nanoparticles are irradiated by light, usually ultraviolet light (UV), with energy equal to or higher than its band gap (>3.0 eV), electrons on the TiO$_2$ surface are excited and will escape from valence band to the conduction band, leading to formation of electron- hole pairs on the surface – excited negative charged electrons in the conduction band and positive charged holes in the valence band. The created pairs can recombine, radiatively or get trapped and react with other materials absorbed on the photocatalyst. The pairs will cause redox reactions at the surface, the negative electrons (e$^-$) will combine oxygen to produce super oxide radical anions (O$_2^-$), the positive electric holes (h$^+$) will act with water to generate hydroxyl radicals. Ultimately, all the formed highly active oxygen species will oxidize organic compounds to carbon dioxide (CO$_2$) and water (H$_2$O). Hence, titanium dioxide can decompose common organic matters in the air such as odour molecules, bacteria and viruses. However, it has been demonstrated that the intensity of photocatalytic activity of titanium dioxide is affected by its physical and chemical properties such as crystallinity, shape, size of the particles and surface area. The mechanism of generation of oxidative radicals and photodecomposition of organic compounds could be seen in Fig. 2.1 and Fig. 2.2.

![Fig. 2.1 Schematic of the generation of highly oxidative radicals under UV light at the TiO2 surface](image-url)

2.4 Apply titanium dioxide in textile substrate

Because of the unique advantages of titanium dioxide, great attention has given to apply titanium dioxide on fabrics to create multifunctional surface such as UV protection, antibacterial, self-cleaning. (HASHIMOTO K. et al, 2005) In textile industry, both commercially available titanium dioxide nano-powder (Degussa P25) and titanium dioxide particles synthesised from a precursor via sol-gel method could be used, the textile materials could be cellulose (Moafi H. F. et al,2011), cotton (Mihailovic D. et al ,2011a), protein material such as wool(Tung W.S. and Daoud. W.A., 2008b, 2009a), synthesized material like nylon(Mejía M. I., 2011), PET(Karbownik I. et al, 2009), and their blends(Bozzi A. et al, 2005). To deposit TiO$_2$ on the surface of textile substrate, different techniques could be used, some of them are summarized in the table 2.1

<table>
<thead>
<tr>
<th>Method</th>
<th>Pro.</th>
<th>Con.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol-gel</td>
<td>Could combine different properties at one step; Easy to operate; Homogeneity of product at molecular level</td>
<td>Shrinkage during curing; Instruments should suitable for alcohol; Lack of durability; Impact handle property; Degradation of the carrier</td>
<td>Uddin M.J et al, 2007; Mihailovic D. et al, 2011a,b; Mejía M. I., 2011; Tung W. S and Daoud W.A., 2008b, 2009a,b; Montazer M. et al, 2011a,b,c; Bozzi A. et al, 2005;</td>
</tr>
<tr>
<td>Technique</td>
<td>Advantages</td>
<td>Disadvantages</td>
<td>References</td>
</tr>
<tr>
<td>--------------------</td>
<td>----------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>Grafting</td>
<td>Stable and durable product as introduction of coupling agent; No degradation of the carrier; Most uniform deposition</td>
<td>Pre coating is necessary for better adhesion; May cause toxic wastes</td>
<td>Daoud W.A. et al, 2005a,b; Wu D. et al, 2009; TEXTOR T., 2009; Qi K. and Xin J. H., 2010</td>
</tr>
<tr>
<td>Sputtering</td>
<td>Fast deposition; Take place at low temperature;</td>
<td>Poor adhesion as no chemical bonds, only Van Der Waals, diffusion, mechanical interaction</td>
<td>Xu Y. et al, 2009, 2010, 2012; Amor S.B. et al, 1998a,b; Carneiro J.Q. et al, 2007; Wei Q. et al, 2009</td>
</tr>
<tr>
<td>Layer by layer</td>
<td>Easy to operate, uniform deposition, less energy and instrument input</td>
<td>No covalent bonds formed</td>
<td>Uğur Ş.Ş. et al, 2010, 2011; Liu J. et al, 2012; LU P. and DING B., 2009</td>
</tr>
<tr>
<td>Hydrothermal method</td>
<td>Same as sol-gel method</td>
<td>Same as sol-gel method</td>
<td>Zhang H. et al, 2012;</td>
</tr>
<tr>
<td>Ultrasonic irradiation</td>
<td>a fast, simple, and inexpensive one-step reaction; not involve any toxic materials</td>
<td>Poor adhesion due to no covalent bonds formed</td>
<td>Perelshtein I. et al, 2012</td>
</tr>
<tr>
<td>Bi-component</td>
<td>Less chemical involved; Less energy consuming; One step process; Stable and durable product</td>
<td>Limited functional material on the fabric surface; Limited function; Degradation of the carrier may occur</td>
<td>Lim S. K. et al, 2012;</td>
</tr>
<tr>
<td>Method</td>
<td>Characteristics</td>
<td>Decreased effects</td>
<td>References</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------------------------------------------------------------------------</td>
<td>------------------------------------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Melt mixing</td>
<td>Less chemical involved; Less energy consuming; One step process; Stable and durable product</td>
<td>Decreased mechanical property; Aggregation of functional material on the fabric surface; Limited function; Degradation of the carrier may occur</td>
<td>Kuo F.C.J. et al., 2012a, b; Todorov L.V. and Viana J. C., 2007; Huang Y.P. et al, 2007; Hong G. B. and Su T.L., 2012;</td>
</tr>
<tr>
<td>Electrospinning</td>
<td>Big surface area; Inherent functional; Stable and durable product</td>
<td>For non woven; Decreased mechanical property; Degradation of the carrier may occur</td>
<td>Han X. J. et al, 2012;</td>
</tr>
</tbody>
</table>

Table 2.1: summary of methods

However, even different methods were used to deposit TiO$_2$ on fabrics, but generally all the methods mentioned in the table could be divided into two categories: functional finishing or coating, which creates a functional surface on the material by coating or finishing process, includes sol-gel, sputtering, hydrothermal method, grafting and ultrasonic irradiation methods.

The other category is blending, includes bi-component, melt mixing, electrospinning, this category could be further divided into blending during melt spinning or during in situ polymerization. Blending during spinning means mixing TiO$_2$ nano particles with PET melt during spinning; blending during polymerization means adding TiO$_2$ nano particles in polymerization solution to form PET granules containing TiO$_2$.

### 2.4.1 Functional Coating or finishing

In the coating and finishing field, a dip-pad-dry-cure process is mostly used and the sol-gel method is the most popular method because its unique advantages (DAOUD W.A. and Xin J.H., 2004). In order to improve efficiency of the photocatalytic degradation, many efforts have been made. The main focuses were the improvement of photocatalytic activity in visible range of the solar spectrum; the extension of photoactivity life time as the activity will decrease slowly after long time use due to absorption of contaminants; and the improvement of adhesion between the nano particle and its support materials. (Bottcher H. et al, 2010)

The photoactivity of titanium dioxide is depended on the band gap, the band gap of titanium dioxide lies in the UV range (3 eV for rutile and 3.2 eV for anatase), which
takes a small fraction in the solar spectrum. In that case, to improve the photoactivity is to shift the onset of the photocatalytic response from UV light to visible region. The most common strategy studied to obtain this goal is doping. The titanium dioxide could be doped either with noble metal such as gold, silver, platinum, or with non-metal materials such as nitrogen, fluorine. (Chen X. and Mao S., 2007) In textile field, many investigations have been focused on doping TiO$_2$ with noble metals.

Qi K. et al (2011) developed a Fe$^{3+}$ doped nanosized anatase to extend the photocatalytic activity. In their study, they doped the nanosized anatase with different concentrations of Fe$^{3+}$ and applied the doped anatase on cotton to evaluate the self-cleaning property. During their study, they found that the doped anatase showed a strong absorption in UV - visible light and significantly enhance in photocatalytic activity while no effect on the crystal structure of TiO$_2$. In the studies of Mihailovic D. et al (2011c), Dastjerdi R. and Montazer M. (2010, 2011), Tung W. S and Daoud W.A. (2012), similar result of increased antimicrobial efficiency and photodegradation were obtained when doping titanium dioxide with other metals such as silver, boron (B), magnesium (Mg), and cobalt (Co) particles.

When applying nanosized TiO$_2$ on polyester materials, another problem is how to get a good adhesion between the nanoparticles and the support polyester material as there is limited bonding site on the material surface. As TiO$_2$ has a good affinity for carboxyl and hydroxyl groups, but the number of them are very limited on the polyester surface, (Senič Ž. et al,2011) great attention has been given to improve the adhesion between polyester and the nano particles.

In order to have a good adhesion, numerous approaches have been employed as a pretreatment to modify the fabrics surface or nano titanium dioxide surface. The fabric surface are modified to create carboxyl or hydroxyl groups on the surface, which are potential bonding sites with positively charged nanoparticles. Quite a few techniques could be used to functionalize polyester surface, some of them being: plasmas, includes radiofrequency (FR) ( Mihailovic D. et al, 2010a, 2011a,d), microwave (MW), vacuum (Mejia M.I. et al,2009) and low temperature plasma(Qi K.et al, 2007); UV irradiation (Kiwi J. and Pulgarin C.,2010); alkaline (Hashemizad S. et al,2012); enzymes includes protease (Montazer M. et al,2011a,b,c), lipase(Kim H.R. and Song W.S., 2006) and hydrophobins (Opwis K. and Gutmann J.S., 2011) and alginates(Mihailovic D. et al, 2010b).

The titanium surface could be pretreated with surface modifier to graft functional groups onto titanium dioxide surface, thereby improving the affinity of the nanoparticles to the fabric. Sojka-Ledakowicz J. et al (2009) treated nano TiO$_2$ with alkoxyisilane, and then applied the grafted TiO$_2$ onto polyester and cotton fabrics, in their study, they found that polyester was more uniformly covered with aminosilane.
grafted TiO$_2$ and also had an increased photocatalytic activity. On the other hand, the photoreaction induced by titanium dioxide may cause degradation on the support fabric, to suppress this effect, inert shells, which is usually silica (SiO$_2$), was introduced to coat onto TiO$_2$ cores. (Fakin D. et al, 2012; Zhang Y. et al, 2011)

The other most common method used to get good adhesion between the nanoparticles and the fabric is the introduction of covalent linking agent or a electrostatic interaction layer (Matsuzawa S. et al, 2008), the agent could be coupling agent, crosslink agent or a mixture. In the studies of last years, quite a few materials had been used to create bonding between fabric and nano titanium dioxide, some of them being: citric acid (Montazer M. and Hashemikia S., 2012), polysiloxane(Dastjerdi R. et al, 2013), BTCA (1,2,3,4-butane tetra carboxylic acid) (Montazer M. and Pakdel E., 2011c), APTMS and IPTMS(Zhao J. et al,2012), alkoxysilane (Siwińska-Stefańska K. et al, 2011), epoxysilanes, NCC (Nanocrystal cellulose)(Peng X. et al,2012), Silicone and acrylic (Dong Y. et al, 2007). For example, Dastjerdi R. et al (2013) described a method to produce durable functional fabric using crosslink agent polysiloxane. In their research, the authors firstly coated the fabric with nano TiO$_2$ emulsion, after drying the fabric was then immersed in a emulsion containing polysiloxane. Using this process, the TiO$_2$ nano particles were trapped and held by the net formed by crosslinked polysiloxane from dropping off from fabric support. A similar method was applied and evaluated by Mejia M.I. et al (2010).

In order to improvement water fastness of coating of TiO$_2$ on polyester fabrics, Bottcher H. et al (2010) compared the fastness of some often used coupling agent, included aminosilanes, Fixapret CP/BASF- acrosslinking agent based of dimethyoldihydroxyethylene urea, Ebecryl 600/Fluka-an oligomeric crosslinker based of bisphenol-A epoxydiac ylate, Lupamin 509/BASF- a low molecular poly(vinylamine-vinylformamide) copolymer and polymers with reactive terminal epoxyl groups. During their study, the authors found that better result was gained with products containing reactive terminal groups like epoxysilanes. To get the best result, a pre-coating process with epoxysilanes was required. In their study, they demonstrated that the photoactivity of the precoated product remained or even enhanced after 5 wash cycles.

2.4.2 Blending

The titanium dioxide could be added into polymer matrix during in situ polymerization process or during melt spinning process, the melt blending is the most common method and the in situ polymerization process is gaining more attention as it could result in single particle dispersion. (Han K. and Yu M., 2006; Hao L. et al, 2010) When adding nano titanium dioxide particles into some polymers matrix such as poly (ethylene phthalate)(PET), the nano particles tend to aggregate because of the high surface energy, so the surface of nanoparticles is usually necessary to be modified in order to get a good
dispersion (Konagaya S. et al, 2010). Quite a few studies have been focused on achieving good dispersion of titanium dioxide nanoparticles in polymer matrix.

Hao L. et al (2010) studied the in situ polymerization process of incorporating titanium dioxide in PET, they pre-dispersed the nano particle with ethylene glycol (EG) before PET polymerization. During their study, they found that the PH affected significantly on the dispersion of nano particles in EG. And Konagaya S. et al (2010) described that addition of triethylamine (TEA) in the TiO$_2$/EG suspension is highly effective for the dispersion of TiO$_2$ in PET.

In order to improve the miscibility with the polyester matrix, Zhu X. et al (2008) modified the surface of nano TiO$_2$ particles. In their work, they produced 3-Glycidoxypropyltrimethoxysilane (GPS) grafted TiO$_2$ and poly(methyl methacrylate) (PMMA) grafted TiO$_2$, the work indicated that the grafted PMMA enhanced the miscibility between TiO$_2$ and PET. A similar improvement in miscibility was also obtained in the work of Wang Y. et al (2009) when they treated the TiO$_2$ with hexamethyldisiloxane (HMDSO) plasma.

On the other hand, the added titanium dioxide nanoparticles will affect the mechanical properties of the nanocomposite fibres obtained by blending process. Cho D.H. (2004) described that PET yarns containing low TiO$_2$ concentrations (no more that 1100 ppm) had no significant effect on the mechanical properties compared with that of pure PET yarn. But according to Han K. and Yu M. (2006), mechanical properties such as tensile strength and break elongation of the PET/TiO$_2$ fibre decreased with the increase of the TiO$_2$ concentration, and along changes in crystallinity and optical properties. However, Esthappan S. et al (2012) illustrated that mechanical properties of polypropylene fibres were increased by adding TiO$_2$ nano particles. Besides that, Wei Q. (2007) described great attention is needed to get an even distribution of the nano particles in the polymer matrix.

2.5 Poly(lactic acid) (PLA)

Poly (lactic acid) (PLA) is linear crystalline thermoplastic aliphatic polyester made of lactic acid (Farrington D. W. et al, 2010), it is a carbon-neutral bio-plastic because it could be synthesized from agricultural renewable sources. Using melt spinning method, PLA could be made into various types of fibers. In textile industry, PLA fibres are extensively researched due to the low cost of the raw material, biodegradable property and good mechanical properties of the fibre. The fibre properties are relatively similar to those of polyester (PET) fibres. PLA is primarily hydrophobic, however, it more hydrophilic than polyester (PET). It has better moisture absorbency and wicking properties compared with PET. (MOCHIZUKI M., 2010)
During the last decades, because of the unique advantages, the PLA has great potential to replace the conventional polymers synthesized from fossil fuel (Lee S.H. and Song W.S., 2012). It has been widely used in textile field, it could be used to produce geo-textiles, industrial fabrics, home furnishing and garment. Because the moisture management property, garment made of PLA has more comfortable feel. (MOCHIZUKI M., 2010)

2.6 Poly(lactic acid) (PLA) degradation

PLA etching is to degrade the surface material to have a desired surface structure. Different mechanisms, chemical or biological, could be involved in during this process, or a combination of those could also happen during the degradation. A lot of factors such as the chemical structure, surface conditions will affect the etching process. (Tokiwa Y. and Calabia B.P., 2006)

Both chemical and enzymatic degrade PLA via a surface erosion mechanism, which indicated only the surface material will be degraded without changing the bulk properties. (Tsuji H. et al, 2006) For enzymatic degradation, the enzymes used for degradation could be generally classified into lipase type and protease type. Lipase types are primarily used for poly(D-lactic acid)(PDLA) degradation, the protease type are mainly used to degrade poly (l-lactic acid)(PLLA), but not poly(D-lactic acid)(PDLA). (Kawai F. et al, 2011)
3. Material

In this chapter, materials used in this project are presented. During this project, all materials and chemicals were used as received without any further purification.

3.1 PLA

PLA Polymer 3051D (NatureWorks), it is a semi-crystalline pellet, the specific gravity is 1.24g/cm$^3$, glass transition temperature is between 55°C-65°C, the crystalline melt temperature is between 145°C-155°C and melt temperature is 200°C. The melt index is 10-30 g/10min (190°C/2.16K).

PLA Polymer 4042D (NatureWorks), it is delivered in pellet form with melt temperature at 210°C.

PLA Polymer 6201D (NatureWorks), it is a thermoplastic fiber-grade resin derived from annually renewable resource, consisting of 98.6% L-Lactic acid and 1.4% D-lactic acid in weight percent. It is available as a semi-crystalline pellet with the specific gravity of 1.24g/cm$^3$, the glass transition temperature is between 55°C-60°C and the melt temperature is between 160°C-170°C. The melt index is 15-30 g/10min(210°C). The typical process temperatures are 220°C-240°C.

3.2 Titanium dioxide

Titanium (IV) oxide (TiO$_2$) (P25, SIGMA ALDEICH), it is nanosized powder with 21 nm in diameter; the surface area is 35-65m$^2$/g. The molecular weight is 79.87g/mol and the relative density is 4.26g/ml at 25°C.

3.3 Enzyme

Proteinase K (P2308, SIGMA ALDEICH), it is extracted from engyodontium album. It is delivered in lyophilized powder form, the protein content is no less than 90% and the specific activity is ≥ 30 units/mg of protein. This enzyme is typically used at pH 7.5-8.0 at temperature range of 20°C-60°C. The incubation times could be between 30 min to 18 hours.

3.4 Chemicals

2M HCl solution, 2M NaOH solution, Trizma base(Sigma), Na$_2$HPO$_4$(Sigma), sodium azide(Sigma), Methylenle blue(GFS Chemicals).
4. Method

This chapter is divided into three parts, method of sample production, method of etching treatment and property characterisation.

4.1 Sample production

Before sample production, the PLA used as raw material in this project was determined. After selection of raw material, master batch was prepared and then samples were manufactured.

4.1.1 Raw material selection

In order to facilitate the formation of fibre, it is necessary for the raw material to have a reasonably low viscosity. To determine which raw material, among the three available PLAs in this project, a Rheometer (Physica MCR500) was used measure the viscosity of the PLAs. During the test, the shear rate range was 0.01-100 l/s, the test was taken at 230°C in nitrogen condition; during the test, material was put in a gap between a upper plate and a pan. The gap was 1mm and 25mm in diameter. The plate and pan was cleaned after each test. The weight of sample needed was calculated by:

\[ W = V \cdot \rho \]
\[ V = \pi \cdot r^2 \cdot d \]

Where: W is weight.
V is volume.
r is radius of the upper plate.
d is the gap between the upper plate and the pan.

4.1.2 Master batch production

Master batch was produced by Coperion compounder (ZSK 26K) in Swerea IVF. The parameters of the compounder were: diameter of screws was 26mm; screw speed was 230r/min; feeding temperature was 165°C; feeding speed of PLA was 4Kg/hour; feeding speed of nano titanium dioxide powder was 1 Kg/hour; speed of titanium dioxide feeding screws was 200r/min; speed of PLA feeding screws was 400r/min. Before compounding, the titanium dioxide was dried at 100°C for 14 hours and the PLA was dried at 80°C for 4 hours. The compounder was cleaned by polyethylene. After compounding, the master batch was cooled by water and chopped into granulate by a Scheer (Reduction Engineering GMBH).

4.1.3 Prototype production

To be able to facilitate the following test, also because of the limitation of facility, instead of fibre, film about 3cm in width was made as prototype samples in this project. Compared with fibre, the thin film had several advantages and could contribute to more correct result for the following measurements. First of all, it was necessary to have a certain surface area for later measurement; secondary, as the facility limitation, it was impossible to produce fibres with uniform diameter, and slightly difference in
diameter lead to noticeable difference in surface area. Meanwhile, the prototype samples need to be etched, which was heavily depended on the surface area.

The prototype samples were produced by a Micro 15cc Twin Screw Compounder (DSM Research Netherlands) with a 0.4mm film spinneret. Before production, master batch and pure PLA pellet were dried in a vacuum oven (MMM Einrichtungen GMBH) at 65°C for 12 hours. During the production, the screw speed was 100 r/min, the compounding temperature was controlled by three temperature zone on the compounder. The feeding temperature was 190°C, the mixing temperature was 230°C. There was no specific mixing time, the material was feed in the compounder and drew out directly. The samples were cooled by air.

![Fig. 4.1 Schematic of prototype production](image)

4.2 Etching treatment

In order to have a good photocatalytic function, it was necessary to maximise the amount of titanium dioxide exposing on the surface by removing the surface PLA via etching or degradation. There were different methods available to etch and degrade the surface PLA. In this project, different methods were used and compared to etch or degrade the surface PLA.

4.2.1 Alkaline treatment

Alkaline approach is a conventional and effective method for PLA degradation. During the test, weight loss was calculated and used as a function to evaluate the degradation of PLA. The weight loss was calculated by:

\[ W_{\text{loss}}(\%) = \frac{W - W_a}{W} \times 100\% \quad (1) \]

Where: W is weight before etching  
\( W_a \) is weight after etching
The process of alkaline etching could be named: one pellet of pure PLA was put in conical flask, together with 5 ml alkaline solution. The flask was then put in a water bath with slow shaking (80 r/min), the test was taken at 37℃. After the test, the pellet was rinsed with water, the pellet was dried at ambient temperature before and after etching. During the test, weight loss in solutions with different NaOH concentration and different processing time were measured, the detailed information could be seen in table 5.1.

4.2.2 Enzymatic treatment

4.2.2.1 Buffer making

1.5 M Tris-HCl buffer: 1.5 mol Trizma base (Sigma) was dissolved in 800 ml MilliQ water, then adjust the pH to 8.6 with HCl, add MilliQ water to 1L. 

30 mM Tris-HCl buffer: 3.634g (0.03 mol) Trizma base (Sigma) was dissolved in 800 ml MilliQ water, then adjust the pH to 8.6 with HCl, add MilliQ water to 1L.

20 mM Phosphate buffer, 1.42g (0.01 mol) Na₂HPO₄ was dissolved in 400 ml MilliQ water, then adjust the pH to 8.0 with 20 mM HCl, add MilliQ water to 500 ml.

4.2.2.2 Procedure

For enzymatic treatment, the method described by MacDonald R.T. et al (1996) was followed with modifications, named:

For 1.5 M Tris-HCl buffer, one pure PLA pellet was placed in conical flask containing 5 ml buffer, 1 mg proteinase K and 1 mg sodium azide. The flask was covered with cotton ball and put in water bath. The temperature of the water bath was maintained at 37℃ and the samples were slowly rotately shaked at 80 r/min during the whole process. Before and after the experiment, the PLA was dried at ambient temperature. The procedure was same for 30 mM Tris-HCl and phosphate buffers except that for 30 mM Tris-HCl and phosphate buffers, instead PLA pellet, PLA fibre, containing 10% TiO₂ were used and there was no sodium azide put in the solution for the phosphate buffer. After incubation, the samples were rinsed with ice water to stop the treatment. The detailed information could be seen in tables 5.2-5.4.

4.2.3 Prototype samples etching

For the prototype sample, the 30 mM Tris-HCl buffer was used, the procedure and condition was same as mentioned above. During the prototype etching, instead of fibre or pellet, films with a shape of 1cm×3cm×100µm were prepared and used for enzymatic degradation. For each, 4 pieces of films were put in the conical flask, containing 10 ml buffer, 2 mg proteinase K and 2 mg sodium azide. Meanwhile, instead of calculating the total weight loss as a function, the weight loss of per unit surface area
was used as a function to indicate the degradation of prototype, which could be seen:

\[
W_{\text{loss}} (\mu g/mm^2) = \frac{W_b - W_a}{S_{\text{before}}} \tag{2}
\]

Where: 
- \(W_b\) indicate weight before degradation 
- \(W_a\) indicate weight after degradation 
- \(S_{\text{before}}\) indicate surface area before degradation

Since the thickness was hundred times less than the width and length of the sample, then surface area contributed by thickness could be ignored and the effect on the result caused by thickness could also be ignored. So during the calculation, the surface area caused by thickness was not counted. The detailed information could be found in table A.1.

4.3 Characterisation

In this part, the surface character, thermal behaviour, self-cleaning property and mechanical properties of the prototype samples were measured.

4.3.1 Surface characterisation

To be able to characterize the dispersion of nano titanium dioxide powder in the polymer matrix and the effect of etching. The surface and the cross section of the prototype samples were analyzed by a digital microscope (Nikon, Digital sight). The pictures were taken at a 6.3 times magnification.

4.3.2 Mechanical properties

In order to study how the nano titanium dioxide would affect the polymer mechanical properties, tensile strength and flexural properties of the samples were tested. As the thickness of film was not constant, which could lead to a incorrect result, in order to have a specific result, the samples were prepared carefully.

The samples for mechanical test were prepared by a Micro 10cc injection moulding machine (DSM Research Netherlands) (Fig 4.2). The temperature of injection barrel was 230°C, the unloading temperature was 50°C. The melted mixture was injected in the mould in 5s at 5bar. The mix was then held at 12bar for 30s and cooled down at 12bar for 30s before take out the samples. Before sample preparation, raw materials were dried at 65°C for 12 hours.

4.3.2.1 Tensile strength

The tensile test was taken by a universal testing machine (Elastocom H10KT). The preload was 8N, the speed of test was 10mm/min, the maximum load of the clamp was 5000N. The testing part of the specimen was 4mm in width 2mm in thickness.
specimens were tested for each batch and all the test were conducted at room temperature.

4.3.2.2 Flexural test

Specimen bar with a shape of 4mm×10mm×100mm was put on two supports and a load was applied in the centre, the deformation at break of the sample was measured by three point bending method. The distance between the two supports was 80mm, 3 specimens were tested for each batch and all the test were conducted at room temperature.

4.3.3 Thermal property analysis

To evaluate to what content the thermal properties will be affected by the nano titanium dioxide and the enzymatic degradation, a Differential scanning calorimeter (DSC) and Thermogravimetric analysis (TGA) were taken.

4.3.3.1 Differential scanning calorimeter (DSC)

The DSC analysis was taken by DSC Q1000 (TA Instrument). The weight of all samples were about 10mg. The samples were heated to 200°C at a heating rate of 10°C/min and held for 2min to erase previous heat history (I run), the samples were cooled down to -10°C at the a cooling rate of 10°C/min (II run), the samples were then reheated again to 200°C at the same rate (III run).

4.3.3.2 Thermogravimetric analysis (TGA)

The TGA analysis was taken by TGA Q500 (TA Instrument). The heating rate was 10°C/min, the highest temperature was 600°C and held at that temperature for 2min.

4.3.4 Self-cleaning property evaluation

The self-cleaning property of the sample was evaluated in both quantitative and qualitative ways. The coffee and red wine stains were used to test if the sample could be capable of self-cleaning. Meanwhile, in order to assess the self-cleaning function in a qualitative way, a Methylene blue bleaching test was conducted.
4.3.4.1 Discoloration of stains

Stains of coffee and red wine were used to test the self-cleaning property. Two droplets of coffee or wine were dropped on one piece sample by pipette and dried at ambient temperature. The samples were then irradiated by two 6w UV tubes (VL-206SLS), predominantly wavelength 365 nm. The distance between the sample and the UV lamp was 20 cm. Pictures were taken after certain intervals, the distance between camera and sample was about 5cm. The experiment lasted 10 days. The schematic could be seen in Fig. 4.2:

Fig 4.2 Schematic of self-cleaning, distance between UV light and samples was 20cm

4.3.4.2 Degradation of methylene blue dye

In order to evaluate the photocatalytic activity of the product in a quantitative and qualitative way, the degradation property on methylene blue (MB) in aqueous condition under illumination of UV light (same as used for stains degradation) was detected by a UV-Vis spectrophotometer (LIBRA S60) by measuring the changes in absorption spectra and absorbance at a specific wavelength.
5. Result

This chapter mainly gives part results on sample production, sample treatment and property evaluation. Other original data or results are given in appendix A-G.

5.1 Sample production

In this section, results regarding material selection and sample production are presented.

5.1.1 Material selection

Among the three different polymers available, PLA6201, PLA3051 and PLA4042, the one with the lowest viscosity was the most feasible for this project. After calculation, 0.6g (0.49 cm³) raw material was put in the gap between the upper plate and the pan, the plate and the pan were cleaned after each test. The result could be seen in Fig. 5.1.

![Rheology characterisation of raw materials](image)

Fig. 5.1 Rheology characterisation of raw materials: the test was carried out at 230°C, shear rate range was 0.01-100 l/s. Blue curve indicates PLA6201, red curve for PLA 3051, Green for PLA4042

5.1.2 Master batch and prototype production

During the production of master batch, two kind of master batch were prepared in Swerea IVF, master batch with 20% nano titanium dioxide (labelled as 20% master batch) and master batch with 15% nano titanium dioxide (labelled as 15% master batch). The master batches were compounded at 220°C, the temperature of the feeding zone...
was 165°C, the compounding was a continuous process with a output of 5Kg per hour and no specific mixing time was left.

All film samples were made by compounding pure PLA and the 15% master batch at 230°C, except the one with 20% titanium dioxide concentration. The ratio between the pure PLA and master batch was determined according to the final prototype needed in this project. In the end, five different kinds of films, varying in titanium dioxide concentration, were prepared. They were pure PLA film, film containing 5 wt% TiO₂, film containing 10 wt% TiO₂, film containing 15 wt% TiO₂ and film containing 20 wt% TiO₂, labelled as pure PLA, 5% TiO₂, 10% TiO₂, 15% TiO₂ and 20% TiO₂ respectively in short. The thickness of the films was within the range of 100- 400µm. During the production, no specific compounding time was left.

5.2 Etching treatment

During the test, all samples, both alkaline and enzymatic treatment, were processed at 37°C in water batch with slow shaking (80r/min). The samples were dried and weighted at room temperature.

5.2.1 Etching process selection

For the enzyme treatment, different buffers were introduced and compared in order to get the most suitable way for PLA etching. After calculation of equation (1), the results could be seen in the following tables.

<table>
<thead>
<tr>
<th>Concentration (M/L)</th>
<th>Weight before(mg)</th>
<th>Time(h)</th>
<th>Weight after treatment(mg)</th>
<th>weight loss(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>36.2</td>
<td>2</td>
<td>36.2</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5</td>
<td>41.5</td>
<td>2</td>
<td>40.8</td>
<td>1.69</td>
</tr>
<tr>
<td>1</td>
<td>37.4</td>
<td>2</td>
<td>36.6</td>
<td>2.14</td>
</tr>
<tr>
<td>2</td>
<td>38</td>
<td>2</td>
<td>36.8</td>
<td>3.16</td>
</tr>
<tr>
<td>2</td>
<td>40.6</td>
<td>4</td>
<td>38.7</td>
<td>4.68</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>6</td>
<td>37.2</td>
<td>7.00</td>
</tr>
<tr>
<td>2</td>
<td>43.8</td>
<td>8</td>
<td>39</td>
<td>10.96</td>
</tr>
<tr>
<td>2</td>
<td>45.4</td>
<td>10</td>
<td>39.2</td>
<td>13.66</td>
</tr>
<tr>
<td>2</td>
<td>40.5</td>
<td>20</td>
<td>28.6</td>
<td>29.38</td>
</tr>
</tbody>
</table>

Table 5.1 Weight loss of pure PLA in alkaline solution at 37°C in slow shaking water bath, varying in alkaline concentration and processing time
<table>
<thead>
<tr>
<th>Weight(mg)</th>
<th>Proteinase K weight(mg)</th>
<th>Process time(h)</th>
<th>Weight after treatment(mg)</th>
<th>weight loss(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44.5</td>
<td>1</td>
<td>1</td>
<td>44.5</td>
<td>0</td>
</tr>
<tr>
<td>41.9</td>
<td>1</td>
<td>2</td>
<td>41.8</td>
<td>0.24</td>
</tr>
<tr>
<td>41.3</td>
<td>1</td>
<td>4</td>
<td>41.7</td>
<td>-0.97</td>
</tr>
<tr>
<td>39.3</td>
<td>1</td>
<td>6</td>
<td>39</td>
<td>0.76</td>
</tr>
<tr>
<td>39.5</td>
<td>1</td>
<td>8</td>
<td>39.2</td>
<td>0.76</td>
</tr>
<tr>
<td>38.6</td>
<td>1</td>
<td>20</td>
<td>38.9</td>
<td>-0.78</td>
</tr>
<tr>
<td>37.8</td>
<td>1</td>
<td>24</td>
<td>37.7</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 5.2 Weight loss of pure PLA in 1.5M Tris-HCl buffered solution enzyme solution at 37°C in slow shaking water bath, varying in processing time

<table>
<thead>
<tr>
<th>Weight(mg)</th>
<th>Proteinase K weight(mg)</th>
<th>Process time(h)</th>
<th>Weight after treatment(mg)</th>
<th>weight loss(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.4</td>
<td>1</td>
<td>4</td>
<td>45.4</td>
<td>8.1</td>
</tr>
<tr>
<td>52.6</td>
<td>1</td>
<td>6</td>
<td>46.7</td>
<td>11.22</td>
</tr>
<tr>
<td>54.9</td>
<td>1</td>
<td>8</td>
<td>48.4</td>
<td>11.84</td>
</tr>
<tr>
<td>50.6</td>
<td>1</td>
<td>15</td>
<td>42</td>
<td>17</td>
</tr>
<tr>
<td>49</td>
<td>1</td>
<td>20</td>
<td>39.6</td>
<td>19.18</td>
</tr>
</tbody>
</table>

Table 5.3 Weight loss of PLA containing 10wt% titanium dioxide in 30mM Tris-HCl buffered enzyme solution at 37°C in slow shaking water bath, varying in processing time

<table>
<thead>
<tr>
<th>Weight(mg)</th>
<th>Proteinase weight(mg)</th>
<th>Process time(h)</th>
<th>Weight after treatment(mg)</th>
<th>weight loss(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51.6</td>
<td>1</td>
<td>4</td>
<td>49.6</td>
<td>3.88</td>
</tr>
<tr>
<td>47.9</td>
<td>1</td>
<td>6</td>
<td>46</td>
<td>3.97</td>
</tr>
<tr>
<td>53.7</td>
<td>1</td>
<td>8</td>
<td>51.2</td>
<td>4.66</td>
</tr>
</tbody>
</table>

Table 5.4 Weight loss of PLA containing 10 wt% titanium dioxide in 20mM phosphate buffered enzyme solution at 37°C in slow shaking water bath, varying in processing time

### 5.2.2 Prototype etching

During the treatment, 4 groups of samples were etched for 2, 4, 6 and 15 hours separately, each group contains 4 samples of each prototype sample batch. During the etching, for samples with same nano filler concentration, the ones needed 2 hours
treatment shared the same incubating solution with that undergone 4 hours degradation. All samples were 1cm×3cm, the thickness was about 100µm, four pieces of each batch were processed. The procedure named: samples were taken out from the incubating conical flask after 2 hours treatment by a tweezers, the samples needed 4 hours etching were then put in the incubating solution and incubated in water bath at 37℃ for 4 hours. Using the same way, the samples of 6 hours treatment shared the same incubating solution with the ones of 15 hours treatment.

After treatment, the samples were dried and weighted in room temperature; weight loss of each sample was calculated. An average weight loss of one piece of sample was calculated and used to evaluate per unit weight loss. The results could be found in table 5.5, the original data could be found in appendix A:

<table>
<thead>
<tr>
<th>Sample</th>
<th>process time(h)</th>
<th>Average weight loss(mg)</th>
<th>Sample</th>
<th>process time(h)</th>
<th>Average weight loss(mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>2 1.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 1.88</td>
<td></td>
<td>5%TiO₂</td>
<td>2 0.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 4.88</td>
<td></td>
<td></td>
<td>4 4.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15 _</td>
<td></td>
<td></td>
<td>6 5.55</td>
<td></td>
</tr>
<tr>
<td>10%TiO₂</td>
<td>2 1.10</td>
<td></td>
<td></td>
<td>2 0.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 4.9</td>
<td></td>
<td>15%TiO₂</td>
<td>4 4.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 5.7</td>
<td></td>
<td></td>
<td>6 5.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15 1.0</td>
<td></td>
<td></td>
<td>15 1.15</td>
<td></td>
</tr>
<tr>
<td>20%TiO₂</td>
<td>2 1.28</td>
<td></td>
<td></td>
<td>_ _</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 5.20</td>
<td></td>
<td></td>
<td>_ _</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 5.88</td>
<td></td>
<td></td>
<td>_ _</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15 1.50</td>
<td></td>
<td></td>
<td>_ _</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.5 average weight loss of one piece of sample after enzymatic treatment, samples undergone 2 and 4 hours treatment shared the same solution, samples undergone 6 and 15 hours treatment shared the same solution.

As mentioned in section 4.5, the surface area contributed by thickness was ignorable, so the surface area of one piece of sample is:

\[ S_{before} = width \times length \times 2 = 10 \times 30 \times 2 = 6 \times 10^2 mm^2 \]

According to the equation (2):

\[ W_{loss} (\mu g/mm^2) = \frac{W_b - W_a}{S_{before}} \]

Here the \( W_b - W_a \) indicates the average weight loss in table 5.5. Then per unit weight loss could be obtained by putting the data in the equation, which could be seen in table 5.6.
<table>
<thead>
<tr>
<th>Sample</th>
<th>process time(h)</th>
<th>Per unit weight loss(μg/mm(^2))</th>
<th>Sample</th>
<th>process time(h)</th>
<th>Per unit weight loss(μg/mm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>2</td>
<td>2.83</td>
<td>5%TiO(_2)</td>
<td>2</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.13</td>
<td></td>
<td>4</td>
<td>7.79</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>8.13</td>
<td></td>
<td>6</td>
<td>9.25</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>_</td>
<td></td>
<td>15</td>
<td>2.04</td>
</tr>
<tr>
<td>10%TiO(_2)</td>
<td>2</td>
<td>1.75</td>
<td>15%TiO(_2)</td>
<td>2</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8.21</td>
<td></td>
<td>4</td>
<td>8.17</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>9.54</td>
<td></td>
<td>6</td>
<td>9.04</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1.67</td>
<td></td>
<td>15</td>
<td>1.92</td>
</tr>
<tr>
<td>20%TiO(_2)</td>
<td>2</td>
<td>2.13</td>
<td></td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8.67</td>
<td></td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>9.79</td>
<td></td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>2.50</td>
<td></td>
<td>_</td>
<td>_</td>
</tr>
</tbody>
</table>

Table 5.6 per unit weight loss of one piece of sample after enzymatic treatment, samples undergone 2 and 4 hours treatment shared the same solution, samples undergone 6 and 15 hours treatment shared the same solution.

5.3 Characterisation

In this part, results of the properties of the prototype samples are presented.

5.3.1 Surface characterisation

Pictures of enzymatic treated and untreated samples were taken by digital microscope with 6.3 times magnification, the thickness of all samples was about 100µm. Pictures of surface and cross section of pure PLA and 20%TiO\(_2\) could be seen in Fig 5.2-5.5, others could be seen in appendix B.

![Fig. 5.2 Cross section of pure PLA: a) before enzymatic degradation; b) after 6 h enzymatic degradation;](image)
Fig. 5.3 Surface of pure PLA with about 500pixel in width, 1pixel =0.26mm; a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation

Fig. 5.4 Surface of 20% TiO₂ with about 500pixel in width, 1px =0.26mm: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation
Fig. 5.5 Cross section of 20% TiO$_2$: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation

### 5.3.2 Mechanical properties

During the tensile and flexural test, three specimens of each batch prototype were tested, 8N pre-load was applied and the speed of the clamp was 10mm/min. The table 5.7 shows the average values of result, the original data could be found in appendix C.

<table>
<thead>
<tr>
<th>E-Modulus(Mpa)</th>
<th>Pure PLA</th>
<th>5% TiO$_2$</th>
<th>10% TiO$_2$</th>
<th>15% TiO$_2$</th>
<th>20% TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile (Mpa)</td>
<td>3003.87</td>
<td>4043.77</td>
<td>4293.17</td>
<td>4551.4</td>
<td>4799.35</td>
</tr>
<tr>
<td>Elongation at yield(%)</td>
<td>3.12</td>
<td>2.42</td>
<td>1.88</td>
<td>1.59</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Table 5.7 Result of tensile strength

Three points method was used to measure the flexural property, the sample for test was placed on two support points, the gap between the two supports was 8cm, a load was applied in the centre of the specimen to deform the specimen, the speed of the deformation was 10mm/min.

<table>
<thead>
<tr>
<th>Pure PLA</th>
<th>5% TiO$_2$</th>
<th>10% TiO$_2$</th>
<th>15% TiO$_2$</th>
<th>20% TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flex strength(Mpa)</td>
<td>107.64</td>
<td>108.76</td>
<td>119.59</td>
<td>91.04</td>
</tr>
<tr>
<td>Strain at break(%)</td>
<td>5.46</td>
<td>4.77</td>
<td>3.57</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Table 5.8 Result of flexural test

### 5.3.3 Thermal property analysis

In this part, thermal behaviours of the samples are presented. The results are presented in groups depending on concentration of titanium dioxide, the individual result could be found in appendix D and E.
5.3.3.1 Differential scanning calorimeter (DSC)

During the DSC test, about 10mg sample was put in aluminium pan for measurement. Every sample was heated twice to 200°C at a heating rate 10°C/min, between the two heating processes, the sample was cooled down to -10°C at the cooling rate of 10°C/min. The results could be seen in following figures; only the cooling and reheating processes were shown since the first heating process stated the thermal history, which was not necessary for analysis. Detailed information for each sample could be found in appendix D.

Fig. 5.6 DSC result for samples before enzymatic etching
Fig. 5.7 DSC Result of pure PLA samples before and after enzymatic etching

Fig. 5.8 DSC Result of 20% TiO₂ samples before and after enzymatic etching
5.3.3.2 Thermogravimetric analysis (TGA)

During the TGA test, about 10mg sample was put in a platinum plate for test, samples were heated to 600 °C and held for 2min. The platinum plate was tared before each test, after each test the plate was cleaned by alcohol burner. All samples, except samples undergone 2h enzymatic etching, were tested. The result could be seen in the following figures, more detailed data could be found in appendix E.

![Fig. 5.9 TGA result for samples before enzymatic etching](image-url)
Fig. 5.10 TGA Result of pure PLA samples before and after enzymatic etching

Fig. 5.11 TGA Result of 20% TiO$_2$ samples before and after enzymatic etching
5.3.4 Self-cleaning property assessment

In this part, the results of the self-cleaning property on stains of coffee, red wine and methylene blue are presented.

5.3.4.1 Decolouration of stains

During the test, two drops of coffee or red wine were dropped on sample, dried at room temperature. The samples were then irradiated by UV light whose wavelength was 365nm. Pictures were taken after 0, 3,7,10 days. The following figures show how the stain changes in colour. The result could be seen in table 5.9, only samples undergone 6 hours enzymatic etching were shown in the table, one non enzymatic etched 20%TiO₂ sample was taken as the reference, for other samples could be seen in appendix F.

<table>
<thead>
<tr>
<th>Decolouration of coffee and red wine stains under UV irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Before irradiation</strong></td>
</tr>
<tr>
<td>Reference</td>
</tr>
<tr>
<td>5%TiO₂</td>
</tr>
<tr>
<td>10%TiO₂</td>
</tr>
<tr>
<td>15%TiO₂</td>
</tr>
<tr>
<td>20%TiO₂</td>
</tr>
</tbody>
</table>

Table 5.9 Decolouration of coffee and red wine stains under UV irradiation
5.3.4.2 Degradation of methylene blue (MB)

The test was carried out in aqueous conditions since it was impossible to have a homogeneous coating on the plastic sample. During the test, two pieces of 1 cm x 3 cm samples were put in a 50 ml beaker containing 10 ml methylene blue solution. The initial concentration of methylene blue was 2 mg/L. The distance between UV lamp and the sample was 20 cm. Absorption spectra were measured after 3 h, 7 h and 24 h irradiation. The solution before UV irradiation was taken as reference, absorption spectra of tap water was also used as a reference to evaluate to what extent the sample could degrade the methylene blue.

During the test, the start wavelength was 400 nm and ended with 700 nm with a 4 nm bandwidth. Part of the result could be seen in the following figures, detailed information could be found in appendix G. Only two groups of samples, the one with highest (the samples undergone 6 hours enzymatic etching) and the one with lowest weight loss (the samples undergone 15 hours enzymatic etching) were measured.

Fig. 5.12 UV-vis absorption spectra of MB solution, for 5% TiO₂ samples with the highest weight loss after enzymatic treatment

Fig. 5.13 UV-vis absorption spectra of MB solution, for 10% TiO₂ samples with the highest weight loss after enzymatic treatment
Fig. 5.14 UV-vis absorption spectra of MB solution, for 15% TiO\(_2\) samples with the highest weight loss after enzymatic treatment

Fig. 5.15 UV-vis absorption spectra of MB solution, for 20% TiO\(_2\) samples with the highest weight loss after enzymatic treatment
Fig. 5.16 UV-vis absorption spectra of MB solution for 20%TiO$_2$ samples with the lowest weight loss after enzymatic treatment

The absorbance of 664nm wavelength after different irradiation time could be seen in table 5.10.

<table>
<thead>
<tr>
<th>Irradiation time(h)</th>
<th>5%TiO$_2$</th>
<th>10%TiO$_2$</th>
<th>15%TiO$_2$</th>
<th>20%TiO$_2$</th>
<th>water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.337</td>
</tr>
<tr>
<td>3</td>
<td>-0.11</td>
<td>-0.098</td>
<td>-0.137</td>
<td>-0.121</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-0.156</td>
<td>-0.188</td>
<td>-0.22</td>
<td>-0.222</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>-0.23</td>
<td>-0.312</td>
<td>-0.327</td>
<td>-0.332</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Irradiation time(h)</th>
<th>5%TiO$_2$</th>
<th>10%TiO$_2$</th>
<th>15%TiO$_2$</th>
<th>20%TiO$_2$</th>
<th>water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.337</td>
</tr>
<tr>
<td>3</td>
<td>-0.079</td>
<td>-0.13</td>
<td>-0.185</td>
<td>-0.11</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-0.133</td>
<td>-0.233</td>
<td>-0.264</td>
<td>-0.266</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>-0.282</td>
<td>-0.331</td>
<td>-0.337</td>
<td>-0.305</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.10 Changes in absorbance of MB solution during the photodegradation process.
6. Discussion and analysis

In this chapter, the results presented in this report will be analyzed and discussed.

6.1 Prototype production

In this part, the reasons why the raw material was selected and the production of master batch and prototype will be presented and discussed.

6.1.1 Material selection

PLA 6201D (Nature work) is the most suitable raw PLA material, among the raw materials available in this project. When applying the same shear rate at 230°C, all the materials showed a Newtonian behaviour when the shear rate was low, the viscosity turned into non-Newtonian with increase in shear rate, the viscosity decreased dramatically when it became non-Newtonian. During the test, the PLA 6201D was the last one became non-Newtonian and also the one with lowest viscosity. When applying a shear rate of 0.1 1/s, the viscosity of the PLA 6201D was 232 Pa·s, the numbers were 341 Pa·s and 715 Pa·s respectively for PLA 3051D and PLA 4042D. The shear stress and shear rate had a linear relation when the viscosity appeared Newtonian behaviour and became non-linear when the viscosity became non-Newtonian.

During melt spinning process, polymers with low viscosity could facilitate the formation of fibre as low viscosity leads to low shear stress during extruding. Therefore the PLA 6021D was decided to use as the raw material for the whole project.

6.1.2 Master batch and prototype production

During the master batch compounding, the PLA and nano titanium dioxide were fed with different feeder, however, because the fluffy character of the nano titanium dioxide powder, it may cause the nano powder stuck in the feeder, which should be avoided during the compounding.

During the production of prototype samples, films of 2-3cm in width, instead of fibre, was decided to be produced due to several advantages mentioned in section 4.1.3. However, the parameters were set up according to that of fibre production, so it could also used to produce fibre. During the film production, it was observed that the film was not flat, but flat on edges and swelling in the centre part. That indicates the fluid had different velocity when passing through the spinneret, the fluid in the central of the spinneret had the highest velocity and the velocity decreased progressively towards to the spinneret wall. This phenomenon was caused by shear stress as the middle of spinneret has the lowest in the centre and increases progressively, reaching maximum at the spinneret wall.
During the production of master batch and prototype samples, special attention should be paid on compounding time. PLA tend to thermal degrade when exposing to high temperature and it should be avoided in during compounding. The thermal degradation of PLA could be easily identified by colour; the PLA became dark yellowness or brown when thermally degraded. During compounding, to eliminate the thermal degradation as much as possible, no extra mixing time, except the time materials passing through the extruder, was left during sample production and an air cooling system was introduced. The torque caused by friction between material and screw during compounding would transferred into heat and may leaded to thermal degradation of material connecting the screw, however, no degradation was observed when the speed of screws was 250 r/min during master batch production, during the sample production, screw speed no more than 250 r/min would also not cause thermal degradation, but because of the limitation of facility, it made it very difficult for material feeding and also tend to excess the capability of the compounder when the screws speed higher than 100 r/min. So screws speed was set at 100r/min during sample production.

The thickness of the film was controlled by outputting speed together with drawing speed of the film. In order to facilitate the following measurement, the final sample should be thin, by controlling the speed of outputting and drawing, films with thickness within the range of 100 to 400µm were prepared.

6.2 Etching

6.2.1 Alkaline treatment

For the Alkaline treatment, as could be imagined, both concentration and processing time affected the etching result. As could be seen in Table 5.1, for solutions varying in alkaline concentration, after 2 hours processing, no weight loss was observed of sample etched in 0.1M sodium hydroxide solution. From 0.1M sodium hydroxide solution to solution with the highest alkaline concentration, the weight loss almost linearly related to the alkaline concentration and the sample etched in 2M sodium hydroxide solution had the highest weight loss, a 3.16% loss in weight was observed after 2 hour etching.

Table 5.1 also gives information on the relation between processing time and weight loss, from 2 to 10 hours, a almost linear relation could be found between the weight loss and processing time. The weight loss from 3.16% after 2 hour etching increased to 13.66% after 10 hours etching. The etching speed tended to accelerate after 10 hour, increased to 29.38% weight loss after 20 hour. That may caused by many factors such as surface area, impurities on the surface. But generally, it could be concluded that the alkaline method is a effective way for PLA degradation and the etching property of alkaline solution could last for at least 20 hours.
6.2.2 Buffer selection

For enzymatic etching, the result depends on the activity of enzyme, a lot of parameters have effect on the enzyme activity. Among them, PH, temperature and buffer were regarded as the most important parameters. To see which buffer lead to a better etching result, different buffers were evaluated and the results are presented in tables from 5.2 to 5.4, using weight loss as a function of evaluation.

For 1.5M Tris-HCl buffer, after incubating 24 hours, no change in weight was observed, which indicated the proteinase K did not active in this condition.

In order to update information and to see if the enzyme degrade PLA containing titanium dioxide, fibres containing 10 wt% titanium dioxide were used in 30mM Tris-HCl buffered and 20mM phosphate buffered solution.

For samples etched with 0.3mM Tris-HCl buffered solution and phosphate buffered solution, the result is shown in table5.3 and 5.4.

For samples etched in 0.3 mM Tris-HCl buffered solutions, within a period of 20 hours, an almost linear relation between processing time and weight loss was observed. The weight loss climbed from 8.1% after 4 hour incubation to 19.18% after 20 hours incubation. As the weight loss was increasing with increase in processing time, thus firstly it could be concluded that the proteinase K in 30mM Tris-HCl buffered condition could degrade PLA containing titanium dioxide, and secondly, it could also be induced that the etching activity of proteinase K could last for 20 hours for fibres containing 10% titanium dioxide.

For samples incubated in phosphate buffered solutions, a similar tendency was also observed. The weight loss increased from 3.88% after 4 hour incubation to 4.66% after 8 hours incubation.

When comparing the etching process of 30mM Tris-HCl buffered solution and 20mM phosphate buffered solution, it could be easy to tell that compared with phosphate buffered solution, within a period of 8 hours, samples in 0.3mM Tris-HCl buffered solution had much more weight loss, had a 11.84% weight loss, about 3 times than that of samples in phosphate buffered solution, which indicated samples in 30 mM Tris-HCl buffered solution had a faster etching speed. In this case, it could be induced that the enzyme proteinase K had a higher activity in 30mM Tris-HCl buffer than in 20mM phosphate buffer. The difference in enzyme activity may because the difference in PH, the PH of the former buffer was 8.6 and that for the later one was 8, or because the concentration of the buffer was different. Besides that, it may also because different chemicals in the buffer had different impact on the enzyme activity.
6.2.3 Etching process selection

Based on the information mentioned above, that the alkaline treatment, compared with enzymatic method, was a faster and more effective approach. For the enzymatic approaches, proteinase K in 30mM Tris-HCl buffer gave the best result. From this point, it seemed that the alkaline treatment was the most suitable solution for this project. However, the alkaline treatment causes a lot of environmental problems, so, in this project, from the eco-friendly viewpoint, proteinase K in 30mM Tris-HCl buffer was selected for final prototype etching.

6.2.4 Prototype etching

For prototype etching, for samples containing same nano filler, the samples undergone 2 etching hours shared the same solutions with the ones of 4 hours treatment, the process named: the samples needed 2 etching hours were etched in the solution and taken out from the incubating solution by a tweezers after 2 hours; the samples needed 4 etching hours were then put in the solution. Using the same procedure, the samples undergone 6 etching hours shared the same solution with the ones of 15 hours.

As can be seen in table 5.6, after 2 hours enzymatic etching, pure PLA had the greatest per unit weight loss, followed by 20% TiO₂, the weight loss of 5% TiO₂ and 15% TiO₂ ranked the last and they almost had the same weight loss after 2 hours etching. About 1.8μg/mm² between the highest and the lowest samples was calculated. That difference might be caused by a lot of factors such as thickness, surface characterisation of the samples and incubation conditions.

For samples undergone 4 and 6 hours enzymatic etching, it was observed that 20%TiO₂ lost more weight than other samples, reached 9.79μg/mm² after 6 hours treatment. Compared with samples undergone 2 hours treatment, the weight loss for most samples increased dramatically except pure PLA, take the 15%TiO₂ as a sample, the number increased from 1.08μg/mm² to 8.17μg/mm², with a growth of 7.09. The situations for other TiO₂- contained samples were similar. That indicated during the period from 2 to 4 hours, the etching speed of TiO₂- contained samples accelerated, meanwhile, the speed for pure PLA slowed down. Since the samples undergone 2 and 4 hours shared the same solution, for TiO₂- contained samples, the significantly increase in per unit weight loss might because at the beginning two hours, the etching activity of the proteinase K was not fully activated, the proteinase K became more active after the first 2 hours. May also because after the degradation of the surface PLA, surface connecting to the enzyme was partly PLA and partly TiO₂, which leaded to less PLA area than pure PLA samples, thus more enzyme molecules could be attached on PLA part than that attached on pure PLA samples.

However, from 4 to 6 hours, the increase of per unit weight loss for TiO₂- contained samples was much less than that of pure PLA. Approximately 1μg increase was
observed for TiO$_2$- contained samples and the number was 5μg for pure PLA. This indicated during that period, the etching speed for TiO$_2$- contained samples slowed down but the speed of pure PLA accelerated.

One noticeable thing in the figure is the weight loss of TiO$_2$- contained samples undergone 15 etching hours. It can be seen that compared with others, TiO$_2$- contained samples undergone 15 etching hours had a very low per unit weight loss. Since the samples shared the same solution with samples undergone 6 hours and were etched after them, it indicated that the etching activity of the solution decreased significantly after working for 6 hours. That might be because of the released products of etching decreased the enzyme activity, or changed the condition of the solution which could dramatically impact the enzyme activity.

**6.3 Surface characterisation**

This part mainly focuses on the dispersion of nano titanium dioxide powder in the polymer matrix and how the enzymatic treatment affects the surface of the sample.

**6.3.1 Dispersion of titanium dioxide**

How the nano titanium dioxide dispersed in the polymer matrix affected a lot on properties of the final product. In the polymer matrix, the inorganic nano powders tend to aggregate, the aggregation increases with concentration. To produce a useful product, the inorganic nano powder should have a good dispersion in the polymer matrix. To investigate the dispersion of nano powder in polymer matrix, pictures of the surface and cross section of 6.3 times magnification taken by a digital microscope were analyzed.

As shown in pictures in section 5.3.1 and in appendix B, within an area about 500px in width, for all sample, no obvious aggregations could be observed on surface and cross section, the polymer matrix formed a continuous network with nano titanium dioxide embedded in. It indicated the nano particles dispersed pretty well in the polymer even when the concentration reached 20 wt%.

However, the observation of aggregation of titanium dioxide heavily depended the magnification of the microscope, since the maximum magnification of the microscope was only 6.3. In this case, the aggregation might be too small to observe with this magnification.

**6.3.2 Effect of enzymatic etching**

Form fig. 5.3, it could be seen that after enzymatic degradation, the pure PLA from transparent became into fogged, with increase in etching time, this phenomenon became more obvious, at the same time, the enzymatic etching also lead to a coarse surface.
For samples containing titanium dioxide, as it could be imagined, the enzymatic treatment made the nano titanium dioxide expose on the surface, the amount of nano titanium exposing on the surface depended a lot on the concentration, the higher the concentration, the more nano titanium dioxide exposed on the surface, as could be seen in fig.5.4 and appendix B. The exposed titanium dioxide particles appeared as white dot on the picture. The etching time also affected the amount of nano particles exposing on the surface, longer etching time seemed to lead to more nano particles exposing on the surface, but this was only observed on 20%TiO₂ samples.

From the pictures on the cross section, when comparing the samples with and without enzymatic treatment, no significant difference could be observed, that partly might because of only slight amount of material was taken away from surface and partly because of the limitation of the microscope, as the maximum magnification of the magnification was 6.3, which made it impossible to analyze the characterisation of surface and cross section more detailed.

6.4 Mechanical properties

As could be clearly seen from table 5.7, e-modulus increased with increasing of titanium dioxide concentration, compared with pure PLA, increased the titanium dioxide concentration to 5%, 10%,15% and 20%, the e-modulus increased 34.62%, 42.92%, 51.52% and 59.77% respectively. The elongation at yield had a reverse route, decreased from 3.12% for pure PLA to 1.16% for 20% TiO₂. On the other hand, when the concentration of the nano filler no more than 10%, the tensile strength was almost not affected. contras to the tendency of e-modulus, the tensile strength tended to decrease with the increase of titanium dioxide except the one with 5%. But when increased the concentration from 10% to 20%, the tensile strength decreased from 65.54Mpa to 48.66Mpa, about 25% less than the pure PLA.

For flexural measurement, as shown in table 5.8, increase in nano filler concentration resulted in decrease in strain at break. For pure PLA, a 5.46% strain was measured, the number decreased to 1.76% for 20% TiO₂, decreased by 67.77%. Meanwhile, flex strength at break appeared in a different way. For samples containing no more than 10% titanium dioxide, then flex strength tended to increase with increasing in TiO₂ concentration of, from 107.64Mpa for pure PLA to 119.59Mpa for 10% TiO₂. But the number decreased rapidly for samples containing 15% and 20% TiO₂, became 78.13Mpa for 20% TiO₂, decreased by 27.42% compared with that of pure PLA.

In general, it was obvious that the introduction of a certain degree of nano titanium dioxide into PLA could increase some mechanical properties such as e-modulus, tensile strength and flex strength; at the same time, the introduction of titanium dioxide decreases the flexibility of the polymer.
From the mechanical test, it was possible to get some information the dispersion of the nano filler in the polymer, if the nano filler aggregate seriously in the polymer, it would significantly impact the tensile and flex strength. During the test, when the concentration of the nano filler was no more than 10%, no or only slightly decrease was detected, that might be deduced that the nano filler dispersed better when the concentration was no more than 10%, when the number exceeded, big aggregation formed in the polymer and hence impact the mechanical properties significantly. So that might be an indication that the concentration of the nano filler should no more than 10%.

6.5 Thermal properties

In this part, the effect of the nano filler and the enzymatic etching on the thermal properties will be summarised and evaluated.

6.5.1 Differential scanning calorimeter (DSC)

Little effect of nano titanium dioxide on thermal behaviour of the polymer was observed. The introduction of titanium dioxide had no effect on the glass transition temperature ($T_g$) and melting temperature ($T_m$). For all samples, the glass transition was about 62°C and the melting temperature was about 165°C, indicated the nano particles did not affect the mobility of the macromolecular chain. The only effect was found on cold crystalline temperature; generally, introduction of titanium dioxide decreased the cold crystalline temperature. For samples containing no more than 15%TiO$_2$, with increase of TiO$_2$ concentration, the cold crystallization temperature decreased, from about 120°C to about 105°C, but for 20% TiO$_2$, the cold crystallization temperature was about 110°C. It might due to the nano particles affect the nucleation of the crystallisation.

The effect of enzymatic etching on the thermal behaviour was also investigated and no obviously influence was observed on $T_g$ and $T_m$, which indicated the enzymatic etching did not affect the mobility of the macromolecular chain. However, it did affect the cold crystallisation temperature. For pure PLA, the etching did not have any noticeable effect on the thermal behaviour of the polymer. For TiO$_2$-contained samples, the enzymatic treatment generally caused decrease in cold crystallisation temperature with the exception of 15% TiO$_2$ samples, however, there was no clear relation between the processing time and changes in cold crystallisation temperature was identified.

6.5.2 Thermogravimetric analysis (TGA)

From the pictures in part 5.3.3.2 and appendix E, it could be seen that the introduction of titanium dioxide did affect the degradation behaviour of the PLA. Generally, the added nano particles slightly increased the degradation temperature of the polymer. During the test, pure PLA started to degrade at about 300°C, about 20°C lower than
that of samples containing titanium dioxide. That might be an indication that the nano particles did not catalyze the thermal degradation of PLA, reversely, the nano filler improved the thermal stability of the polymer. At the same time, no clear tendency on how the concentration of nano filler affected the degradation temperature was observed.

Another remarkable thing was the enzymatic treatment did affect the degradation behaviour. After enzymatic treatment, the starting degradation temperature of samples undergone enzymatic treatment tended to decrease compared with the ones without treatment. That might because of the degradation of the surface PLA during enzymatic treatment. Additionally, the residues of samples of same labelled titanium dioxide concentration varied randomly, take the labelled 15%TiO₂ samples for instance, after the TGA test, the residue of sample undergone 4 hours etching almost had the same residue with the one without etching, both of them had residues slightly less than 15 wt%. Theoretically, sample after 4 hours etching should have slightly more residue than the one without treatment since the surface PLA was removed during the etching process. This might be an indication that even the titanium dioxide has been proven dispersed reasonably well in the polymer matrix, but still not homogeneously dispersed.

6.6 Self-cleaning property evaluation

The aim of decolouration of coffee and red wine stain was to get a clue if the prototype samples could work. And degradation of methylene blue is an approach to quantitatively investigate the self-cleaning property.

6.6.1 Decolouration of stains

In order to make the results comparable, all the samples should be irradiated with same distance and also the pictures should be taken at same condition. The distances between the UV light and the samples and that between sample and camera were decided at 20cm and about 5cm respectively.

During the test, if the sample could decompose the stains, the stain colour would fade little by little due to the photoreaction induced by titanium dioxide on its surface, in this case, by observing changes in stain colour, clues on if the sample had self-cleaning property could be obtained.

After 10 days assessment, it was found that no changes in colour was observed on reference samples, for reference samples without nano filler, without enzymatic treatment or without UV irradiation, which indicated that titanium dioxide, enzymatic etching and UV irradiation are essential for the self-cleaning performance. As could be seen in table 5.9 and appendix F.
For coffee stains, after 10 days UV irradiation, no change in colour was observed for all samples, which indicated that the samples could not decompose coffee stain within 10 days. That might due to chemical structure of coffee such as molecular weight.

For wine stain, significantly changes in colour were observed for all enzymatic treated TiO₂-contained samples after 10 days irradiation but generally it was a slow process. Within this testing period, it could been seen that the stain became thin from thick at the beginning and the stain colour faded little by little from dark to light during the test, which might an indication that wine stain was partly decomposed.

From the picture shown in appendix F, there was no remarkable difference in colour was observed between samples undergone different etching time, which might be an indication that 2 hours enzymatic etching process was long enough to expose the nano filler on the surface.

Compared with samples containing 5% titanium dioxide, during the decolouration experiment, no better result was obtained for samples with higher concentration, which might be an indication that 5% was sufficient enough to have the maximum photocatalytic activity, higher concentration did not lead to a higher photocatalytic activity for stain degradation.

However, the analysis was only based on the pictures and the result heavily depended on the quality of the pictures, which might decrease the reliability of the result. So the result only could give a clue on if the prototype had effect on the stains. In order to evaluate the function more scientifically, decolouration of methylene blue could be measured using a UV-vis spectrophotometer.

6.6.2 Degradation of methylene blue (MB) dye

During the test, the MB solution without UV irradiation was taken as reference, the value of absorption spectra of the reference was 0; the absorbance of water was also taken as a reference, the closer the curve toward to that of water indicating the more percent methylene blue was degraded. During the test, the absorbance peak for all samples shifted toward to that of water with increase in UV irradiation time. After 24 hours, the absorption curves for some samples, such as samples shown in Fig. 5.13 and 5.14, almost totally overlapped with that of water, which indicated the methylene blue was totally or partly degraded.

From figures shown in section 5.3.4.2 and appendix G, it could be seen that all samples displayed significantly changes in absorption at wavelength of about 664nm, this indicated, which also had been proven by many researchers such as Yao J.(2010) and Lak A. et al(2012), that methylene blue solution had the maximum absorption at wavelength about 664nm. Then it could be used as a sign of MB concentration level.
after degradation. By measuring the absorbance of 664nm at each time and compared with that value of water, it was possible to quantitatively evaluate degradation ratio of methylene blue. The result could be seen in table 5.10. From the table, it could be concluded that, most samples, except 5% TiO₂, according to changes in absorbance at 664nm, degraded more than 90% MB after 24 hours UV irradiation.

The other noticeable thing was that, for samples containing the same titanium dioxide concentration, the one with higher weight loss during etching process tended to have higher methylene blue degradation. This might be an indication that the samples were not properly etched with very few per unit weight loss.

Among all samples, only 15%TiO₂ underwent 6 hours etching reached the same absorbance with that of water after 24 hours irradiation, which indicated the methylene blue was totally degraded during that period. Followed by 10%TiO₂ with the same etching time, had a 98% decrease in absorbance. For the 20%TiO₂ samples, the one with lower weight loss had slightly higher MB degradation ability, which might be caused by tolerance of the equipment during the test.
7. Conclusion

In this report, it has been proven that it is possible to combine nano titanium dioxide into poly (lactic acid) (PLA) polymer via melt blending method but the concentration of the nano filler should not be very high-10% might be the limits in order to make the product have a reasonable mechanical property. And it is also possible etch the product with enzyme to make the nano filler exposing on the surface in order to maximize photocatalytic property.

The concentration of the nano filler and enzymatic treatment of the sample affects the properties in different aspects. Certain amount of nano filler could enhance some mechanical properties but decreased the flexibility of the polymer. Enzymatic etching affected some thermal and surface characterisation of the sample.

During the test of coffee and red wine stains, no obvious changes in colour was observed for coffee stain, however, significantly changes in stains caused by red wine was observed. During the degradation test of methylene blue, most samples, except samples containing 5% titanium dioxide, could degrade more than 90% methylene blue. 15%TiO$_2$ undergone 6 hours etching gave the best result, which totally degraded the methylene blue within 24 hours under UV irradiation.

8. Further development

During this project, the author has investigated some properties, but as there were limitations of time and facility, some further researches could be continued to perfect the final product.

Since the limitation of the light microscopy, it was impossible to totally characterise the dispersion of titanium dioxide in the polymer matrix. To get a better understand on how the titanium dioxide disperse or aggregate in the polymer, it will be valuable to do a scanning electron microscope (SEM) evaluation.

The antibacterial property was not evaluated in this project due to limits of time and equipment, it will be good if investigation could be done regarding this issue in future.

The application of this product was not properly discussed and investigated, to make the product could really industrial valuable, the applications should be further studied.
Acknowledgement

At the end, I would like to sincerely express my thanks to everyone that helped me. My special thanks to my inspiring supervisors, Anders Persson and Prof. Vincent Nierstrasz, thanks them for the inspired meetings tht leaded me in the right direction. The same thanks to my classmate, Karin Rundqvist, for the discussion during report writing. I also would like thank Nils-Krister Persson for providing me material, and I also would like to thank Haike Hilke, Kristina Laurila for the help in polymer and chemical laboratory.

Last, many thanks to my family friends for the encouragement during the whole project.

Chengjiao Zhang
Reference


Daoud Walid A., Xin John H. and Yi-He Zhang, 2005, Surface functionalization of cellulose fibers with titanium dioxide nanoparticles and their combined bactericidal activities, *Surface Science*, 599 , pp. 69-75

Dastjerdi Roya and Montazer Majid, 2010, A review on the application of inorganic nano-structured materials in the modification of textiles: Focus on anti-microbial properties, *Colloids and Surfaces B: Biointerfaces*, 79, pp. 5-18


Feng Lin, 2006, Preparation and Characterization of Polymer TiO2 Nanocomposites via In-situ Polymerization, Master, University of Waterloo


Kawai Fusako, Nakadai Kosuke, Nishioka Emiko, Nakajima Hajime, Ohara Hitomi, Masaki Kazuo and Iefuji Haruyuki, 2011, Different enantioselectivity of two types of poly(lactic acid) depolymerases toward poly(L-lactic acid) and poly(D-lactic acid), *Polymer Degradation and Stability*, 96, pp 1342-1348


## Appendix A: Enzymatic etching

<table>
<thead>
<tr>
<th>concentration of TiO$_2$(%)</th>
<th>process time(h)</th>
<th>weight(mg)</th>
<th>weight after treatment (mg)</th>
<th>weight loss(mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>2</td>
<td>23.4</td>
<td>21.8</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.4</td>
<td>16.7</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>23.4</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.1</td>
<td>21.2</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>22.5</td>
<td>20.6</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.4</td>
<td>26.1</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26</td>
<td>24.4</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24.1</td>
<td>22.4</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>20.5</td>
<td>15.5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.5</td>
<td>24.8</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.7</td>
<td>22.4</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.6</td>
<td>16.1</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>27.7</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.4</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25.7</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.6</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>5% TiO$_2$</td>
<td>2</td>
<td>22.3</td>
<td>21.9</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.4</td>
<td>22.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24.1</td>
<td>23.7</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>38.1</td>
<td>37.3</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>22.2</td>
<td>17.3</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.2</td>
<td>12.1</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.8</td>
<td>17.4</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23.3</td>
<td>20</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>33.8</td>
<td>28.8</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.6</td>
<td>15.8</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.2</td>
<td>16.4</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>38.9</td>
<td>33.3</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>22.4</td>
<td>21.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22</td>
<td>20.8</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.9</td>
<td>21.5</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.8</td>
<td>19.4</td>
<td>1.4</td>
</tr>
<tr>
<td>10% TiO$_2$</td>
<td>2</td>
<td>37</td>
<td>35.9</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25.2</td>
<td>24.1</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.8</td>
<td>25.8</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>39.1</td>
<td>38.1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>15% TiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>--------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>27.2</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.5</td>
<td>18.1</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>43.5</td>
<td>38</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40.3</td>
<td>35.3</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.1</td>
<td>24.3</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>29.6</td>
<td>23.8</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>46.5</td>
<td>41.1</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.9</td>
<td>17</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.8</td>
<td>38.1</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.9</td>
<td>33.5</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.4</td>
<td>33.4</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40.3</td>
<td>39.4</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>33.8</td>
<td>33.1</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>26.6</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.6</td>
<td>26.6</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.7</td>
<td>34.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26.7</td>
<td>21.5</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.8</td>
<td>27.6</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.5</td>
<td>22.1</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>32.8</td>
<td>28</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.9</td>
<td>30.1</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>33.7</td>
<td>28.3</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.6</td>
<td>24.9</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.1</td>
<td>25.3</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.1</td>
<td>23.9</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.9</td>
<td>27</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>28.3</td>
<td>27.1</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26.9</td>
<td>25.6</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28.7</td>
<td>27.2</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>35.8</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35.6</td>
<td>34.5</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.8</td>
<td>29.5</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.8</td>
<td>29.2</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>32.6</td>
<td>28.5</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>37.1</td>
<td>32</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.1</td>
<td>28.1</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>39.2</td>
<td>32.8</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.7</td>
<td>32.8</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>44.7</td>
<td>39.5</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35.2</td>
<td>29.2</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>32.5</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>20% TiO₂</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>28.5</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>37.1</td>
<td>32</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>34.1</td>
<td>28.1</td>
<td>6.0</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>39.2</td>
<td>32.8</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>38.7</td>
<td>32.8</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>44.7</td>
<td>39.5</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>35.2</td>
<td>29.2</td>
<td>6.0</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>32.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Appendix B: Surface and cross section

Table A.1 Original data of enzymatic etching

<table>
<thead>
<tr>
<th></th>
<th>27.2</th>
<th>25.7</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>29.7</td>
<td>28.5</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>32.5</td>
<td>30.7</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Fig. B.1 Surface of pure PLA film with 500px in width, 1px =0.26mm: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation

Fig. B.2 Cross section of pure PLA: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation
Fig. B.3 Surface of 5% TiO₂ with about 500px in width, 1px = 0.26mm: 
a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation

Fig. B.4 Cross section of 5% TiO₂: 
a) before enzymatic degradation; b) after 2 h degradation; 
c) after 4 h degradation; d) after 6 h degradation
Fig. B.5 Surface of 10% TiO$_2$ with about 500px in width, 1px =0.26mm: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation

Fig. B.6 Cross section of 10% TiO$_2$: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation
Fig. B.7 Surface of 15% TiO$_2$ with about 500px in width, 1px = 0.26mm: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation

Fig. B.8 Cross section of 15% TiO$_2$: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation
Fig. B.9 Surface of 20% TiO$_2$ with about 500px in width, 1px = 0.26mm: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation

Fig. B.10 Cross section of 20% TiO$_2$: a) before enzymatic degradation; b) after 2 h degradation; c) after 4 h degradation; d) after 6 h degradation
# Appendix C: Data of mechanical test

<table>
<thead>
<tr>
<th>Product</th>
<th>E-Mod MPa</th>
<th>Elong at Yield %</th>
<th>Tensile MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>3149.4231</td>
<td>2.99000001</td>
<td>65.34375</td>
</tr>
<tr>
<td>Pure PLA</td>
<td>2884.35205</td>
<td>3.019999981</td>
<td>62.25</td>
</tr>
<tr>
<td>Pure PLA</td>
<td>2977.84302</td>
<td>3.359999895</td>
<td>67.40625</td>
</tr>
<tr>
<td>5% TiO₂</td>
<td>4213.03906</td>
<td>2.563999891</td>
<td>64.4375</td>
</tr>
<tr>
<td>5% TiO₂</td>
<td>4511.88086</td>
<td>2.24000001</td>
<td>67.96875</td>
</tr>
<tr>
<td>5% TiO₂</td>
<td>3406.40503</td>
<td>2.46399987</td>
<td>64.21875</td>
</tr>
<tr>
<td>10% TiO₂</td>
<td>3799.87109</td>
<td>2.03999996</td>
<td>65.91666</td>
</tr>
<tr>
<td>10% TiO₂</td>
<td>4258.29102</td>
<td>2.032000065</td>
<td>70.1875</td>
</tr>
<tr>
<td>10% TiO₂</td>
<td>4821.35791</td>
<td>1.404000044</td>
<td>56.22916</td>
</tr>
<tr>
<td>15% TiO₂</td>
<td>4865.80811</td>
<td>1.74399958</td>
<td>65.66666</td>
</tr>
<tr>
<td>15% TiO₂</td>
<td>4276.979</td>
<td>1.27199955</td>
<td>48.125</td>
</tr>
<tr>
<td>15% TiO₂</td>
<td>4511.40381</td>
<td>1.748000026</td>
<td>64.83334</td>
</tr>
<tr>
<td>20% TiO₂</td>
<td>4300.59912</td>
<td>1.287999988</td>
<td>51.41666</td>
</tr>
<tr>
<td>20% TiO₂</td>
<td>4788.68311</td>
<td>1.120000005</td>
<td>47.72916</td>
</tr>
<tr>
<td>20% TiO₂</td>
<td>5308.76416</td>
<td>1.075999975</td>
<td>46.83334</td>
</tr>
</tbody>
</table>

Table C.1 Original data of tensile strength

<table>
<thead>
<tr>
<th>Product</th>
<th>Flex Strength MPa</th>
<th>Strain at Max %</th>
<th>Strain at Break %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>108.84</td>
<td>4.494141</td>
<td>5.712891</td>
</tr>
<tr>
<td>Pure PLA</td>
<td>108.24</td>
<td>4.240723</td>
<td>5.859375</td>
</tr>
<tr>
<td>Pure PLA</td>
<td>105.84</td>
<td>4.505859</td>
<td>4.822266</td>
</tr>
<tr>
<td>5% TiO₂</td>
<td>110.76</td>
<td>4.177734</td>
<td>5.613281</td>
</tr>
<tr>
<td>5% TiO₂</td>
<td>106.68</td>
<td>4.148438</td>
<td>4.275879</td>
</tr>
<tr>
<td>5% TiO₂</td>
<td>108.84</td>
<td>4.35</td>
<td>4.429688</td>
</tr>
<tr>
<td>10%TiO₂</td>
<td>115.08</td>
<td>3.04541</td>
<td>3.164063</td>
</tr>
<tr>
<td>10%TiO₂</td>
<td>124.05</td>
<td>4.012207</td>
<td>4.038574</td>
</tr>
<tr>
<td>10%TiO₂</td>
<td>119.64</td>
<td>3.480469</td>
<td>3.52002</td>
</tr>
<tr>
<td>15%TiO₂</td>
<td>91.68</td>
<td>2.446289</td>
<td>2.455078</td>
</tr>
<tr>
<td>15%TiO₂</td>
<td>89.64</td>
<td>2.285156</td>
<td>2.285156</td>
</tr>
<tr>
<td>15%TiO₂</td>
<td>91.8</td>
<td>2.402344</td>
<td>2.402344</td>
</tr>
<tr>
<td>20%TiO₂</td>
<td>72.75</td>
<td>1.692188</td>
<td>1.692188</td>
</tr>
<tr>
<td>20%TiO₂</td>
<td>79.65</td>
<td>1.846875</td>
<td>1.846875</td>
</tr>
<tr>
<td>20%TiO₂</td>
<td>81.99001</td>
<td>1.739063</td>
<td>1.739063</td>
</tr>
</tbody>
</table>

Table C.2 Original data of flexural strength
Appendix D: Data for DSC

Fig. D.1 DSC Result of 5%TiO₂ samples before and after enzymatic etching

Fig. D.2 DSC Result of 10%TiO₂ samples before and after enzymatic etching
Fig. D.3 DSC Result of 15% TiO₂ samples before and after enzymatic etching

Appendix E: TGA

Fig. E.1 TGA Result of 5% TiO₂ samples before and after enzymatic etching
Fig. E.2 TGA Result of 10% TiO$_2$ samples before and after enzymatic etching

Fig. E.3 TGA Result of 15% TiO$_2$ samples before and after enzymatic etching
Appendix F: Decolouration of stains

Fig. F.1 Samples with 5\% TiO\textsubscript{2}, the enzymatic etching time could be seen on the top of each picture: a, e, i) before UV irradiation; b, f, j) after 3days irradiation; c, g, k) after 7days irradiation; d, h, l) after 10days irradiation

Fig. F.2 Samples with 10\% TiO\textsubscript{2}, the enzymatic etching time could be seen on the top of each picture: a, e, i) before UV irradiation; b, f, j) after 3days irradiation; c, g, k) after 7days irradiation; d, h, l) after 10days irradiation
Fig. F.3 Samples with 15% TiO₂, the enzymatic etching time could be seen on the top of each picture: a, e, i) before UV irradiation; b, f, j) after 3 days irradiation; c, g, k) after 7 days irradiation; d, h, l) after 10 days irradiation.

Fig. F.4 Samples with 20% TiO₂, the enzymatic etching time could be seen on the top of each picture: a, e, i) before UV irradiation; b, f, j) after 3 days irradiation; c, g, k) after 7 days irradiation; d, h, l) after 10 days irradiation.
Appendix G: Methylene blue degradation

Fig. G.1 UV-vis absorption spectra of MB solution, for 5% TiO₂ samples with the lowest weight loss after enzymatic treatment

Fig. G.2 UV-vis absorption spectra of MB solution, for 10% TiO₂ samples with the lowest weight loss after enzymatic treatment
Fig. G.3 UV-vis absorption spectra of MB solution, for 5%TiO₂ samples with the lowest weight loss after enzymatic treatment.
THE SWEDISH SCHOOL OF TEXTILES
UNIVERSITY OF BORÅS

Address: Skaraborgsvägen 3, Borås, S-501 90
Web: http://www hb se/en/The-Swedish-School-of-Textiles/