PROPERTIES AND EFFECTS OF CROSSLINKED POLYMER ON STARCH AND POLYLACTIC ACID BLEND

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PROPERTIES AND EFFECTS OF CROSSLINKED POLYMER ON STARCH AND POLYLACTIC ACID BLEND

ABSTRACT

The blend of starch and PLA possessing the excellent properties of plastic products and its complete degradability has been a hot research topic in recent years. In the experiment, 7 experimental samples are made by applying the method of melting the blend of polylactic acid, starch and trimethylchlorosilane in different proportions and the mechanical properties, optical analysis and water absorption tests are conducted respectively. The changing trend of various properties of polylactic acid and starch at different mass ratios is analyzed as well as the influence of addition of trimethylchlorosilane on the properties of the composite.

It is found that with the increase of starch content, the mechanical properties of the composites decreases (tensile strength, young modulus and elongation at break all decrease), the absorbability decreases and the water absorption increases. The FTIR analysis shows that the addition of trimethylchlorosilane does not substantially change the composition and structure of the blend system of starch / polylactic acid. The changes only occurred on several peak absorptions, which also leads to the changes in mechanical properties, adsorbability and absorbency.

Keywords: PLA, starch, cross-linked, property

SIFAT DAN KESAN PENYILANGAN POLIMER TERHADAP KANJI DAN ‘POLYLACTIC ACID BLEND’

ABSTRAK

Gabungan kanji dan PLA yang memiliki sifat produk plastik dan tahap biodegradasi yang sangat baik merupakan topik penyelidikan yang hangat beberapa tahun kebelakangan ini. Dalam eksperimen ini, tujuh sampel eksperimen telah dibuat dengan menggunakan kaedah mencairkan campuran asid polylactic, kanji dan trimethylchlorosilane dalam kadar yang berlainan. Sifat mekanik, analisis optik dan ujian penyerapan air turut dijalankan. Aliran yang berubah-ubah kepada pelbagai sifat asid polylactic dan kanji pada nisbah jisim yang berbeza turut dianalisis serta pengaruh penambahan trimethylchlorosilane pada sifat-sifat komposit.

Peningkatan kandungan kanji telah menunjukkan sifat-sifat mekanik komposit menurun (penurunan terhadap kekuatan tegangan, modulus muda dan pemanjangan), proses penyerapan berkurangan dan penyerapan air meningkat. Analisis FTIR menunjukkan bahawa penambahan trimetil chlorosilane tidak banyak mengubah komposisi dan struktur sistem campuran kanji / polylactic acid. Perubahan hanya terjadi pada beberapa penyerapan puncak, yang membawa perubahan pada puncak intensiti. Penambahan tersebut telah menyebabkan perubahan pada sifat mekanikal, penyerapan dan daya kuantiti.

Kata Kunci: PLA, sifat, kesan, penyilangan polimer, kanji

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LIST OF SYMBOLS AND ABBREVIATIONS

% : Percentage

℃ : Degree Celsius

cm : Centimetre

g : Gram

h : Hour

J : Joule

M : Weight of Samples

M : Molar

mg : Milligram

min : Minute

mm : Millimetre

ml : Millilitre

MPa : Megapascal

nm : Nanometre

ppm : Parts Per Million

ASTM : American Society for Testing and Materials

ATR : Attenuated Total Reflection

FTIR : Fourier Transform Infrared Spectroscopy

GC : Gas Chromatography

MFI : Melt Flow Index

ISO : International Organization for Standardization

PBS : Polybutylene Succinate

PHA : Polyhydroxyalkanoate

PLA : Polylactic Acid

PPC	:	Poly Propylene Carbonate
TM		Trademark
TMCS	:	Trimethylchlorosilane
USA	:	United States of America
UV-Vis	:	Ultraviolet-visible
WL	:	Wave Length

LIST OF APPENDICES

CHAPTER 1: INTRODUCTION

1.1 The Research Background

The polymer materials have good functionality and practicality (Brandrup, Immergut, Grulke, Abe, & Bloch, 1989). They play important roles in various fields as they are the third largest type of basic raw materials following wood and steel, which greatly promote the rapid development in the field of science and technology together with the richness of industrial and agricultural production. The polymer materials are also a kind of indispensable materials in our daily life (Coleman & Painter, 2017). However, their extensive use also brings a series of problems that cannot be neglected. Though most traditional polymer materials are refined from petroleum products, the environmental problems caused by production and application have also aroused wide attention with the depletion of petroleum resources and people's increasing awareness of environmental protection. The so-called “white pollution” (caused by non-degradable foamed plastic products) has seriously threatened the ecological environment (Nampoothiri, Nair, & John, 2010). Therefore, it is one of the fundamental ways to solve the problems of environmental pollution and resources depletion through inventing environmentally friendly materials.

Polylactic acid and starch are derived from renewable crops and have excellent quality of biodegradability. Polylactic acid has many similar properties as some general plastics such as polyethylene, polypropylene, and polystyrene and a broader market prospect. It is universally recognized as one of the most promising new packing materials in the new century (Zhang, Shi, Nie, Wang, & Yang, 2012). However, since the current preparation process is too complicated, and the cost is too high, the material is now solely put into use in the medical field. As for the blends of starch and polylactic acid, they do not only have a reasonable price, but also are environmentally friendly since they are reproducible, biodegradable and produce less pollution in comparison with petrochemical raw materials

(Wool & Sun, 2011). This kind of materials is in accordance with the idea of environmental protection and sustainable development strategies.

This aims to investigate the properties of blends of starch and polylactic acid with different contents and the influence of trimethylchlorosilane on the properties of starch and polylactic acid blend.

1.2 Research Objectives

i. To compare different properties of polylactic/starch before and after adding trimethylchlorosilane.

ii. To study the feasibility of application of polylactic/starch and blend of trimethylchlorosilane in wastewater industry (methylene blue is used as adsorbent and simulated as the pollutant; the adsorption capacity of the blend on methylene blue is measured).

1.3 Research Scope

In this study, a number of blend samples are made to analyze the mechanical properties, water absorption and adsorbability of the blend after blending starch with polylactic acid in different proportions. The effects of trimethylchlorosilane on the properties of starch / polylactic acid blend are determined by optical analysis experiment, mechanical analysis experiment and absorbability and water absorption experiment.

1.4 Problem Statement

This aims to investigate the properties of blend consisted of starch and polylactic acid with different content, as well as the impact of trimethylchlorosilane on the properties of the blend consisted of starch and polylactic acid. Besides, in order to prove that the blend containing starch has certain effect on adsorption, two sets of experiments as well as some other simple experimental methods are designed to facilitate better comparisons and obtain some findings.

CHAPTER 2: LITERATURE REVIEW

2.1 The White Pollution and Degradable Material

It is said that human modern civilization has been founded on the basis of fossil energy. However, as these non-renewable resources are increasingly depleting in recent years, it is likely that people will face energy crisis in the near future. On the other hand, people are also suffering from the harms brought by fossil energy, such as severe air pollution, white pollution, etc.

The "white pollution" is a global issue and developing degradable plastics is one of the effective ways to solve this problem. As a kind of synthetic material, plastic has the advantages of light quality, high strength, easy processing and molding and favorable cost performance, which has become an important material indispensable to the production and life. The amount of waste after use is about 50%-60% of the total. The waste plastics have caused great damage to the surrounding environment and formed the so-called "white pollution" (Androniceanu & Drăgulănescu, 2016).

There is no unified standardized definition of the degradable plastics throughout the world, but the definition of degradable plastics according to the standard ASTM D883-92 for plastic terms passed by American Material Laboratory (ASTM) is: in a specific environment, the definition is basically in line with the international standard ISO472 (plastic terms and definitions) for the definition of degradation and cracking (Sawada, 1998).

According to the degradation pathway, the degradable plastics are classified as photodegradable plastics, biodegradable plastics and photo / biological double degradable plastics (Shah, Hasan, Hameed, & Ahmed, 2008). Among them, biodegradable plastics with the complete degradation characteristics and photo / biodegradable plastics with double degradation characteristics are the main research directions at present.

2.2 Biodegradable Plastics

From the view of eco-friendly environment, the advantages of biodegradable plastics are very obvious. Since the production of raw materials and plants are not fossil fuels, a lot of energy can be saved. In addition, emission carbon dioxide is greatly reduced during production (Lambert & Wagner, 2017). Plants will collect carbon dioxide since they are raw materials until the completion of the product. The data show that while 1kg of traditional polypropylene plastics is produced, 3.15kg carbon dioxide is emitted; while 1kg biodegradable plastic is produced, 1.4kg carbon dioxide is emitted. There is no doubt that the future development of biodegradable plastics is very promising.

The biodegradable plastics, including polymer materials, such as polyhydroxyalkanoate (PHA), the materials directly produced by biotechnology and then aggregated, such as polylactic acid (PLA), polybutylene succinate (PBS), polyamino acid, etc; starch based biodegradable plastics, carbon dioxide copolymer aliphatic carbonate ester (PPC), etc (Jayanth et al., 2018). are also included. Among the many biodegradable plastics, PLA, PBS and PPC are the research hotspots in recent years. Together with the starch based biodegradable plastics, they have become the mainstream technologies of the international biodegradable plastics. At present, the technology is relatively mature, the industry scale is large and it is also the main product of the market consumption.

2.3 Polylactic Acid （PLA）

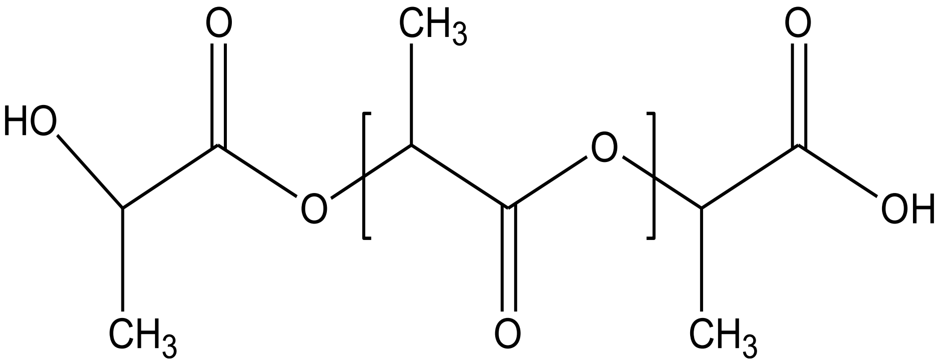

Figure 2.1: Structure of PLA

Polylactic acid is a type of biodegradable polymer produced through the chemical synthesis of lactic acid fermented from renewable plant resources such as grains or plant stalks. Its structure, as shown in Figure 2.1, shows that polylactic acid is nontoxic and irritant. It has excellent biodegradability, biocompatibility and mechanical properties. Meanwhile, it can be processed by traditional methods. Therefore, polylactic acid has become an inevitable trend to replace some existing general petroleum-based plastics. Due to the limitations of its own strength, brittleness, permeability resistance, heat resistance, etc., the application scope of polylactic acid has been restricted. Therefore, the enhancement of modified polyacrylic acid has become one of the hotspots and focus of the research on polylactic acid (Jacobsen, Fritz, Degée, Dubois, & Jérôme, 1999).

Polylactic acid produces no contamination during its productive process and its weight is similar to many engineering plastics. Additionally, it is compatible with organisms. PLA is now widely applied in the traditional fields such as packaging, automobile industry such as doors, rims and seats. It is also widely used in electronic industry such as cases of disc and mobile phone (Graupner, Herrmann, & Müssig, 2009). Today, they are more widely employed in the products such as exfoliative surgical sutures, drug relieving packaging agents, artificial fracture fixation materials, etc(Nampoothiri et al., 2010).

Polylactide (PLA) is synthetic biodegradable polyester which can be completely decomposed into CO_2 and H_2O under the reaction of microorganisms, acids, and alkalis in a short period after being discarded. Its synthetic lactic acid can be obtained from the inexhaustible sugar such as starch, cellulose in nature after the enzymolysis and fermentation rather than depending on petroleum. Lactic acid can even be extracted from molasses which is a by-product of sugar industry or they can also be extracted from whey which is a by-product of dairy industry or sulfite pulp wastes in the paper industry (Drumright, Gruber, & Henton, 2000).

2.3.1 Production of Polylactic Acid

The monomer lactic acid of polylactic acid is common type of metabolite in the biological community. Lactic acid is produced when humans exercise vigorously, as shown in Figure 2.2. In principle, any carbon hydrate can be used to produce lactic acid. In this industry, people usually take advantage of some specific microorganisms to ferment carbohydrates and to form lactic acid, including the extracted cellulose, such as the cellulose extracted from corn and cassava, sugar and straw extracted from sugarcane and sugar beet, which obtains lactic acid by the process of fermentation and dehydration (Auras, Lim, Selke, & Tsuji, 2011; Xiaodong, Xuan, & Rakshit, 1997). The obtained lactic acid needs to be purified to carry out the production of polylactic acid, because the trace fumaric acid and acetic acid in the lactic acid will all cause the termination of the polymerization.

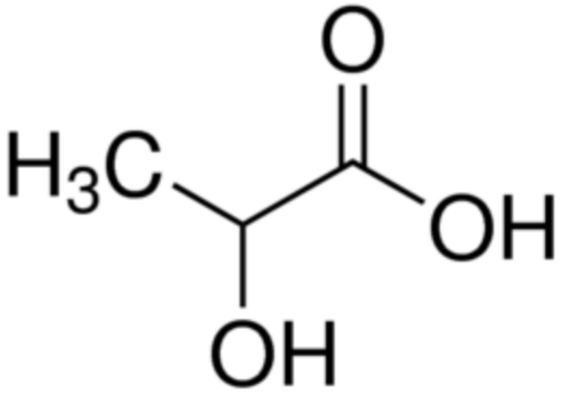

Figure 2.2 Molecular Structure of Lactic Acid

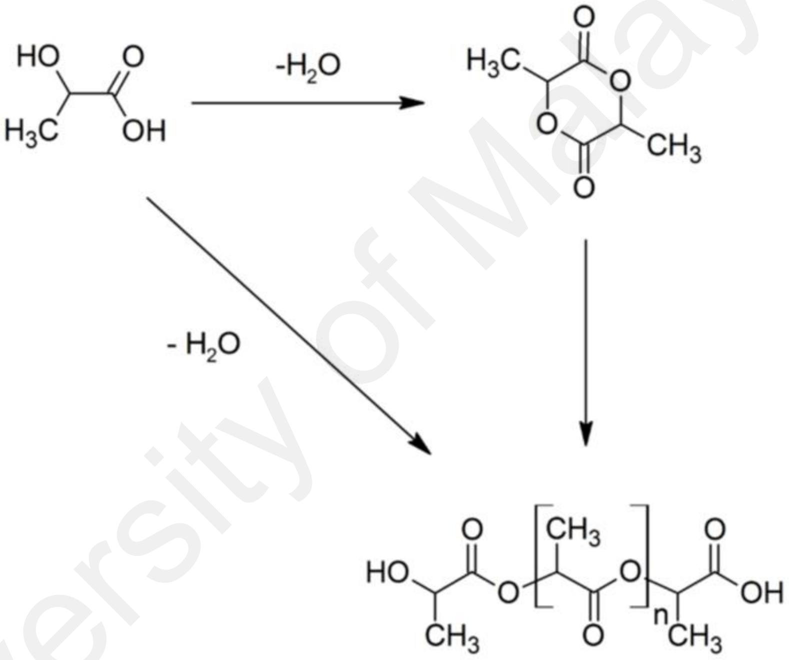

Figure 2.3: Main ways of production of polylactic acid

Polylactic acid can be prepared by the following methods, as shown in Figure 2.3: direct condensation, azeotropic dehydration polycondensation and ring opening polymerization of lactide. Generally speaking, the polylactic acid commercial products with high molecular weight are mainly produced through the ring opening polymerization of lactide (J. Liu, Peizhen, Jiang, & Chen, 2013).

2.3.2 The Property of Polylactic Acid

Polylactic acid （H-[OCHCH3CO]n-OH）has good thermal stability, 170~230 ℃ of processing temperature and good solvent resistance. It can be processed in a variety of ways, such as extrusion, spinning, biaxial tension, injection blow molding. The products made of polylactic acid are biocompatible, glossy, transparent, hand-feeling and well heat-resistant in addition to biodegradation. Polylactic acid (PLA), developed by Guanghua Weiye, has some antibacterial, flame retardancy and UV resistance, therefore, it has a very wide range of uses which is used in packaging materials, fiber and non-woven fabrics, etc and mainly used in clothing (underwear, coat), industry (construction, agriculture, forestry, paper making) and medical and health fields.

PLA is a thermoplastics-type aliphatic polyester resin. PLA is formed through the dehydration synthesis of lactic acid under the appropriate condition. At the normal temperature, it is white powdery solid; the vitrification temperature is 50~60 ℃; the melting point is 170~180 ℃; the density is about 1.25g/cm^3. PLA has favorable biodegradability, compatibility and absorbability.

2.3.3 Applications of Polylactic Acid

Because PLA is a degradable and pollution-free new polymer material, its application prospect is very broad. Most plastic products can be replaced by PLA, but it can not be fully promoted due to the influence of the price factors of PLA products and production technology. Therefore, PLA products are currently applied in high-end application areas, such as biomedicine, etc. (Lunt, 1998)

In the field of biomedicine, there are some side effects in the current use of medical polymer materials, and PLA generates carbon dioxide and water based on its superior biocompatibility and its good physical properties, and there is no harm to the human body.

And there is no need to condutct the second operation for patients with natural degradation. Therefore, PLA can be used for tissue fixation (such as bone screws, fixed plates and suppositories), drug delivery (such as diffusion control), wound dressing (such as artificial skin), and wound closure (such as using sutures, surgical supplies) and so on.

In the field of packaging, the harmless characteristics of PLA can make it widely used in the field of packaging (Sinclair, 1996). It can be used as packing belt, packaging film, agricultural film, tableware and food packaging. The PLA material has a smooth surface, high transparency and good obstacling properties. In some applications, it can take the place of the polystyrene and PET, which greatly reduces the white pollution.

In the field of textiles, PLA can be directly woven into non-woven fabrics by means of spinning or melt blowing, and can also be spun into staple fibers before being made into non-woven fabrics by dry or wet netting (Oksman, Skrifvars, & Selin, 2003). PLA non-woven fabric can be used in agriculture, gardening and other aspects, such as removing weeds with cloths. It can be used as surgical clothing, mask and so on in medical and health aspects. In the field of daily necessities, it can be used as clothes, carpets, children's diapers and so on. In addition, PLA can also be used in the field of household appliances and toy market, such as home appliance shell, rigid packaging, transparent window films, various children's toys, etc.

2.4 Starch

2.4.1 The Property of Starch

The starch is a high polymer of glucose. It is a product of water and carbon dioxide obtained through the photosynthesis by green plants and mainly exists in plants, such as seeds, tuber, etc. The starch has two kinds of structure: linear chain and branched chain. Amylopectin is a non-branched helical structure. Through the structure of amylose and amylopectin, it can be seen that amylose can dissolve in hot water and amylopectin can only expand in hot water but is insoluble in hot water (Zhao, 2013). The structure of amylose is shown in Figure 2.4 and the structure of amylopectin is shown in Figure 2.5.

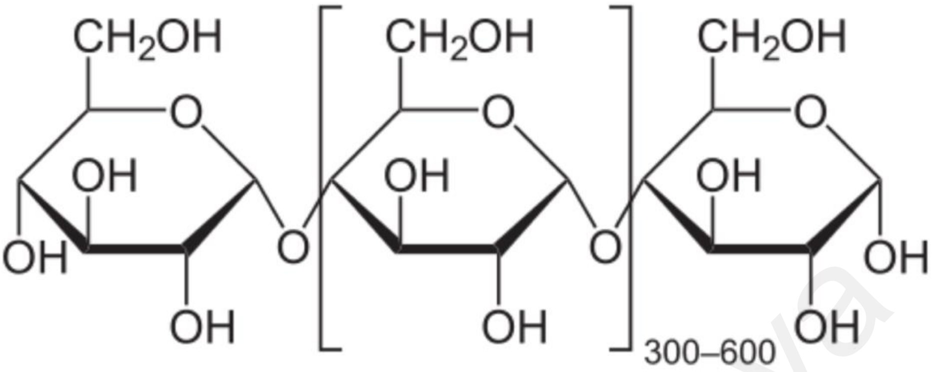

Figure 2.4: The structure of amylose

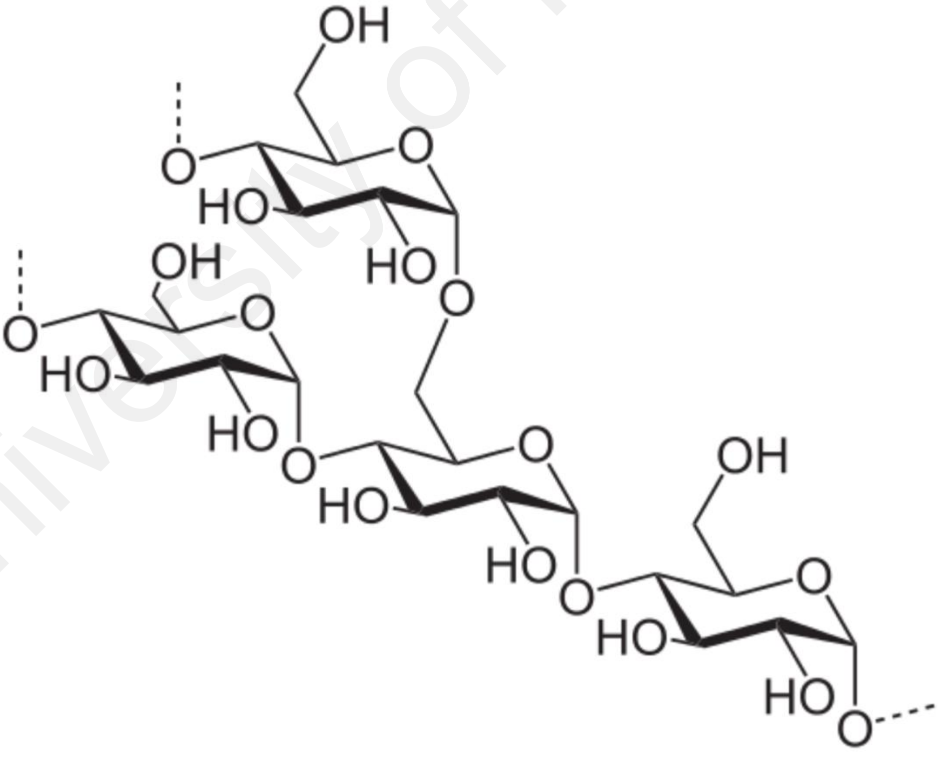

Figure 2.5: The structure of amylopectin

The starch is a kind of rigid high polymer material, because its molecular chain contains hydrogen bonds with strong molecular force, which leads to poor solubility. The melting point and glass transition temperature of starch are both higher than its thermal decomposition temperature. The melting process cannot be observed by direct heating. The pure starch does not have hot workability. Since the machining cannot be realized in the process of making plastic products, the plasticizing modification of starch is particularly important (Jane, 1995).

2.4.2 Applications of Starch

The application fields of starch include: paper making, textile, food processing, adhesive production and other fields (Masina et al., 2017). In the industrial field, paper-making is the largest non-food application in the world, which consumes millions of tons per year (Eliasson, 2004). For example, in a typical copy paper, the starch content can reach 8% of the weight of the paper. Another application of the major category of non-food starches is used in the construction industry, where starch is used in the production of gypsum partition panels. In the field of textiles, the use of starch can produce cleaner products.

In the food industry, high-amylose corn starch can be used to produce weight-loss food and fried food, which is also an ideal food for diabetic patients. It is called "functional food" (L. Liu & Qiao, 2017). In addition, high amylose starch is the ideal food for patients with gallstones and hypertension.

During the production of adhesives, starch is produced modified starch after treated by chemical and physical operation, which changes its viscosity and increases its adhesive strength.

2.5 Trimethylchlorosilane

2.5.1 The Property of Trimethylchlorosilane,

Trimethylchlorosilane, also known as chloro trimethylsilane and abbreviated as TMCS, is the colorless, volatile, flammable liquid, which is soluble in benzene and ether.

Meanwhile, it will be hydrolyzed once encountering water. It is a simple and easily-obtained silicon reagent. Its structure is shown in Figure 2.6. When producing organo-silicon polymer and organic synthesis reactions, it can be used as the intermediate. It can also be used as the powder stock of high molecular polymer, dehydrating agent, high-temperature adhesive and resin desiccant (Thornburg & Bonvallet, 2017).

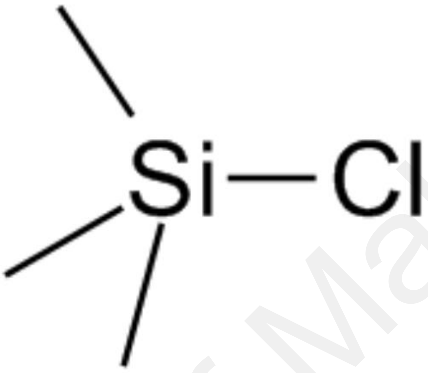

Figure 2.6: The structure chart of trimethylchlorosilane

A series of organic silicides containing silicon functional group can be synthesized by using TMCS as the raw material. The main chemical reactions TMCS can participate in are shown in Figure 2.7.

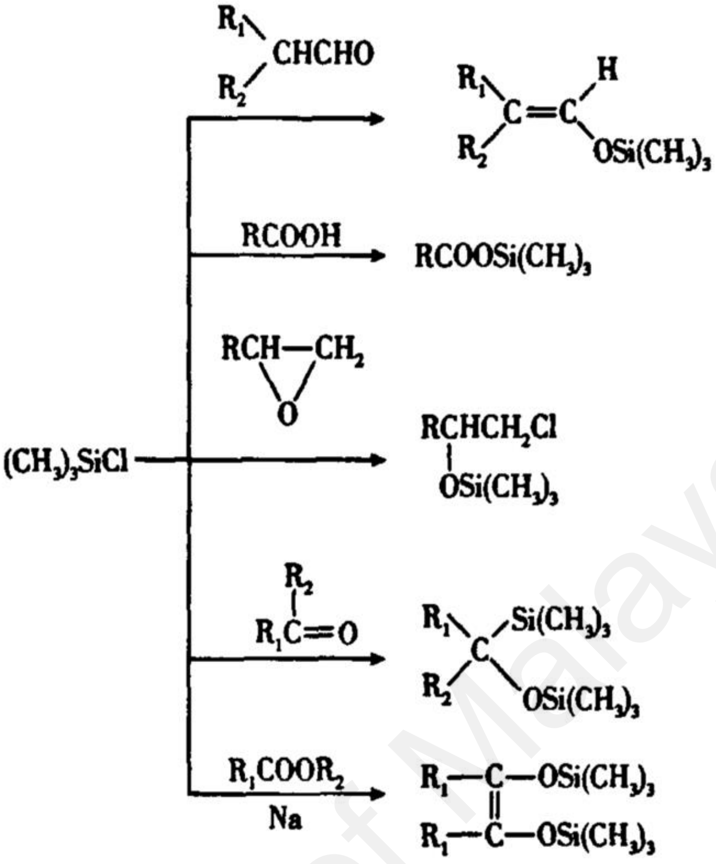

Figure 2.7: The main reaction of the participation of TMCS

2.5.2 Application of TMCS

Trimethylchlorosilane has a very wide range of uses in organic chemistry, which can be not only used as a source of trimethylchlorosilane but also can provide chloride ions when no water. Its main uses are as follows:

Due to the special activity of the silicon-halogen bond, starting from trimethylchlorosilane, a series of organosilicon compounds with silicon functional group structure can be synthesized, such as three methyl alkoxy silane, six methyl two siloxane, six methyl two siloxane, three methyl two siloxane, three methyl cyanosilane, are synthesized from three methyl chloride silane.

Trimethylchlorosilane is an excellent reagent for introducing trimethylchlorosilane into organic molecules., which can be used as a protective group of functional groups such as hydroxyl, carboxyl and amino groups. The reaction of linking and removing trimethylsilyl has high production, mild conditions and wide application, and has been widely applied in organic synthesis.

Silylated derivatives are obtained by the reaction of some biochemical samples with reacted trimethylchlorosilane, which has large volatility, and enables the GC analysis of biochemical samples to be realized.

2.6 The Blend of Starch/PLA/TMCS

Blending PLA with starch can not only ensure the environmentally friendly system but also make up the drawbacks of starch-based plastics in mechanical property and water resistance by utilizing the quality of high intensity and hydrophobic property of PLA. As for the degradable polymers such as microbial synthesis or artificial synthesis with relatively high cost, it is also an effective way to lower the cost by blending starch with them while meeting the prerequisite of its application at the same time (Muller, González-Martínez, & Chiralt, 2017).

Some commercial products have been developed from PLA, such as the Mate-BTM Z series products from Novamont Company (Bastioli, 2001). The mature product of the blend of PLA and starch has not yet developed. The source of PLA is wide and renewable and it is a type of synthetic polyester with the highest development potential. The blending of PLA and starch also has great prospects for the development.

The researcher studies the effect of starch content on the thermodynamics and crystallinity of PLA (Bayer, 2017). The gelatinization of starch with high water content in the blend system will come up and the processing condition has a great influence on the mechanical properties of starch / PLA. The mixer can be used to physically blend it to improve the security of starch / PLA blend system (Sun, 2011).

In recent years, the research on horizontal axis extruders has provided important theoretical basis for polymer processing. The blend of starch/PLA is processed by a twin-screw extruder. The application of the extruder can determine the reaction process and the structure of the product. In the extrusion processing, it is necessary to pay attention to the temperature control of each section. If the temperature is too low, the blend of starch/PLA is not easy to melt, and if the temperature is too high, the blend is prone to be gelatinized, so the temperature control of the extruder is another orientation for study.

The blending of PLA, starch and trimethylchlorosilane is a further guarantee that the system is environmentally friendly while observing whether the trimethylchlorosilane will impact the blend system of PLA and starch.

This research will analyze by observing and explaining a series of comparative experiments. The main task of the experiment is to study and analyze the blend of the above three substances（PLA, Starch, Trimethylchlorosilane）.

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

Polylactic acid （2003D Ingeo TM， melt flow index (MFI) 6g/10 min at 210 ℃ /2.16kg, relative viscosity 4.0, peak melting temperature 145-160 ℃, glass transition temperature 55-60 ℃） was purchased from NatureWorks LLC, USA.Cassava starch was purchased from Thye Huat Chan Sdn Bhd with the size of estimated less than 50 μm. Chlorotrimethylsilane (≥ 99 by area % GC， M=108.64 g/mol， 1L=0.86kg) for synthesis was purchased from Germany.

3.2 Sample Formulation

The composition of the blend sample in the paper is shown in Table 3.1

Table 3.1 Sample Composition

Sample	Content of the sample	PLA	STARCH	TMCS
A	PLA 100%	40g	-	-
B	PLA 97% + STARCH 3%	38.8g	1.2g	-
C	PLA 95% + STARCH 5%	38.0g	2g	-
D	PLA 93% + STARCH 7%	37.2g	2.8g	-
E	PLA 97% + STARCH 3% + TMCS 0.025g	38.8g	1.2g	0.025g
F	PLA 95% + STARCH 5% + TMCS 0.025g	38.0g	2g	0.025g
G	PLA 93% + STARCH 7% + TMCS 0.025g	37.2g	2.8g	0.025g

3.3 Sample Preparation

3.3.1 Mix

Respectively weigh and took the corresponding raw materials according to the above formula (Table 3.1). Then slowly poured the mixture into the mixer (Brabender, Duisburg, Germany). After mixed for 8 minutes at 180°C, it cooled down to the room temperature naturally. The change of mixing temperature and torque with time is shown in Figure 3.1.

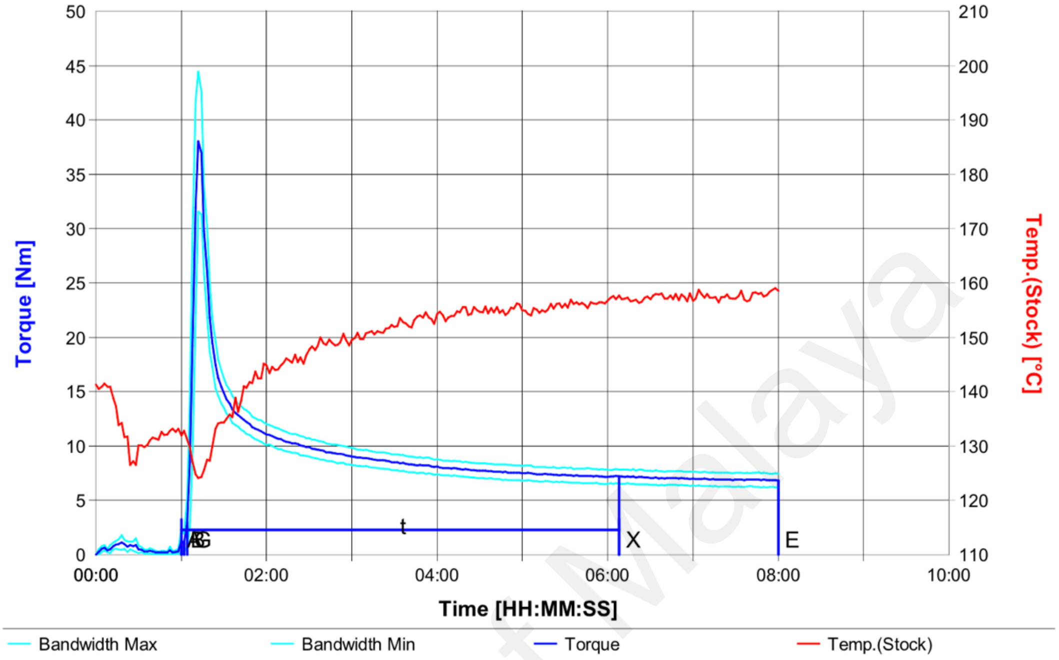

Figure 3.1: BRABENDER® Plastogram PLASTI-CORDER and Mixer Measuring Head Fusion Behavior

3.3.2 Hot Press

I. Place the blends of samples (A-G) in a mold and then put them in the hot press machine (GT-7014-A30C, GoTech, Taiwan). Preheat them at a constant temperature of 180°C for 10 minutes to vitrify the blends.

II. Operat the hot press machine to squeeze the samples at the constant 180 °C, the moment the sample was squeezed by force, it should stop being squeezed so that the sample is not forced. This process should be repeated 6 times and the purpose was to remove the air in the vitrified blend.

III. Keep a constant pressure of 30 MPa at 180°C. The sample was pressed by the hot press machine and squeezed for 3 minutes.

IV. Start the cooling system and cool it for 3 minutes. Then took out the sample of the blend (the sample of blend has a shape of a rectangular with its thickness of about 1-2mm).

V. Place the cooled sample of the blend into the hot press machine again and preheat at the constant temperature of 180°C for 5 min to vitrify the blend again (Mngomezulu, Luyt, Chapple, & John, 2018).

VI. Operate the hot press machine to squeeze the sample at the constant temperature of 180°C, When the sample was squeezed by force, stop squeezing it so that the sample was not forced. This process should be repeated 6 times and the purpose was to remove the air in the vitrified blend again.

VII. Operate the hot press machine to squeeze the sample at a constant 30 MPa pressure at 180°C for 15s.

VIII. Start the cooling system and cool it for 3 minutes. Took out the blend sample. The goal was to press the sample into thin slices so that the relevant experiments could be conducted later.

3.4 Characterization study

3.4.1 Mechanical Properties

The sample cutter（ASTM D638 specimen dimensions）was used for the first time and the dumbbell-shaped standard sample for mechanical experiment was made and the size of standard spline was shown in Figure 3.2.

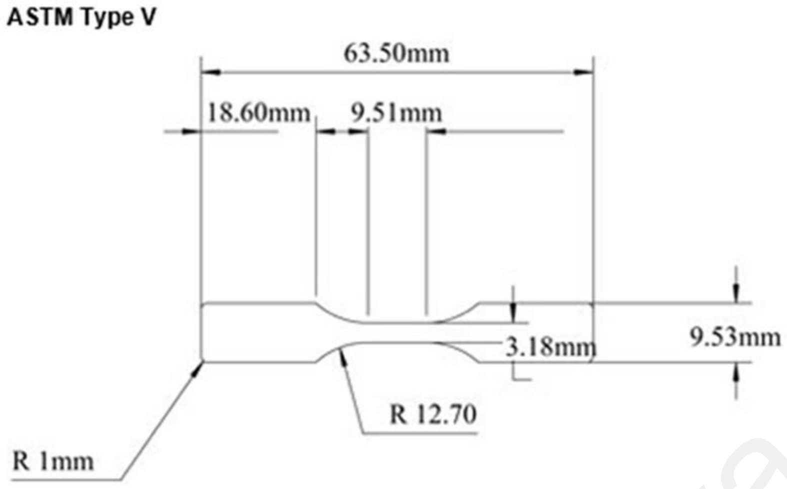

Figure 3.2: the standard sample size

The electricity all-purpose mechanical test machine（Shimadzu AGS-X series tensile machine, Japan）was used to carry out the test. By measuring tensile strength, the elongation and young modulus of each sample were used to make sure whether crosslink can play a certain role in mechanics and the mechanical effect of different content of starch on the blended material.

3.4.2 Spectrophotometer Analysis

Methylene blue is used as adsorbent and simulated as the pollutant. The adsorption capacity of the blend on methylene blue is measured.

Firstly, cut the samples (A-G) to thin rectangles sized 6cm*3cm and place them into 7 beakers. Pour 50 ml 2ppm methylene blue methanol standard solution into each beaker. The whole beaker was wrapped with aluminum foil to prevent sunlight from affecting the experimental result. Start the electromagnetic stirrer, set the speed of 200r/min and waited for 24 hours adsorption. Since the composition of each sample was different, the ability to adsorb methylene blue in the same solution was also different. After a period of time, the sample was taken from the beaker and the adsorbed solution was measured by Spectrophotometer analysis.

Shimadzu UV-2600 ultraviolet-visible (UV-Vis) spectrophotometer manufactured form Japan. Measurements were taken at the wavelength range of 250nm-800nm.

3.4.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Via FTIR Spectrum 400 (Perkin Elmer, USA) using diamond attenuated total reflectance (ATR) technique. The spectra were obtained in a scan range of 450-4000 cm^{-1}, scan rate of 32 units scanned and a $4cm^{-1}$ resolution.

The materials used in the experiment were tested by Fourier transform infrared spectroscopy (FTIR) and the infrared spectra were compared to analyze their interaction situation.

3.4.4 Water Absorption Test

Firstly, the samples (A-G) were cut to thin rectangles with 6cm*3cm sized and placed into 7 beakers. The water is added into 7 beakers, which would be soaked. After 24 hours they would be removed and quickly dried out（using filter paper）. Finally, they would be weighed to provide the convincing evidence of different water absorption capacities.

The average tested values of three sample wafers of each sample would be taken. The calculation formula of water absorption X is as follows:

$$X = \frac{M_X - M_0}{M_0} * 100\%$$

M_X showed the total mass after water absorption and M_0 showed the initial mass of the sample.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 The Mechanical Property Analysis

There are totally 7 samples of the composite materials made through fusing, blending and hot-pressing PLA / starch / thrimethyl chlorosilane of different proportions.

Table 4.1: The average value aggregation of mechanical analysis result

Name	Tensile Strength （MPa）	Young Modulus （MPa）	Elongation at break （%）
Sample A	27.1234±2.4979	1395.13±133.04	4.67893±0.8503
Sample B	33.1093±3.5174	1796.26±87.32	2.2453±0.5025
Sample C	29.4202±1.1645	1644.07±174.64	2.02517±0.275
Sample D	26.9744±3.5985	1483.31±299.7	1.98165±0.3786
Sample E	28.5605±1.8177	1399.77±112.84	3.47105±0.7672
Sample F	24.9624±2.4081	1211.98±72.84	3.44215±0.3759
Sample G	22.8179±1.888	1153.76±124.22	3.20743±1.021

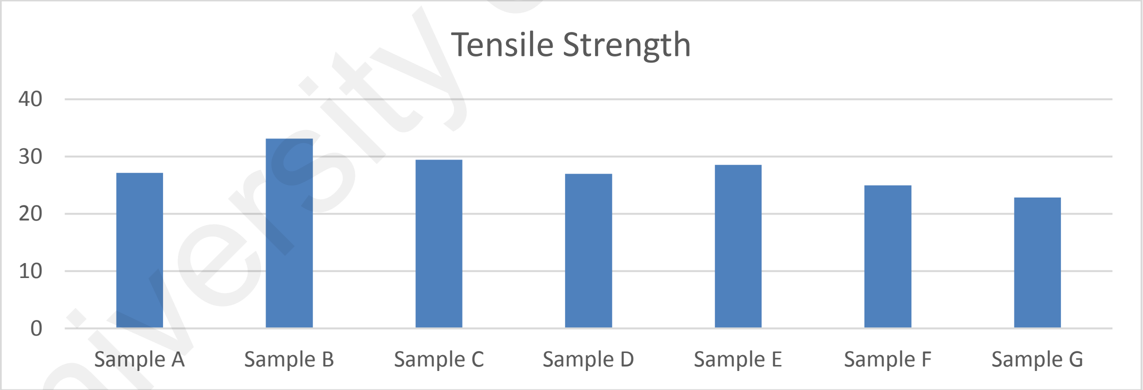

Figure 4.1: Trend chart of Tensile Strength

According to Table 4.1 and Figure 4.1, the tensile strength of starch / PLA blend shows a decreasing trend with the increase of starch content. The value of tensile strength decreases from 33.1093MPa to 26.9744MPa by comparing the blend with starch content accounting for 3% with that accounting for 7%.

In the starch / PLA blend with 0.025g thrimethyl chlorosilane added respectively, the trend of tensile strength still decreases with the increase of starch content. In the presence of thrimethyl chlorosilane, the value of tensile strength decreases from 28.5605MPa to 22.8179MPa by comparing the blend with starch content accounting for 3% with that accounting for 7%.

Therefore, by comparing the starch / PLA blend of same content, the addition of thrimethyl chlorosilane decreases the value of tensile strength.

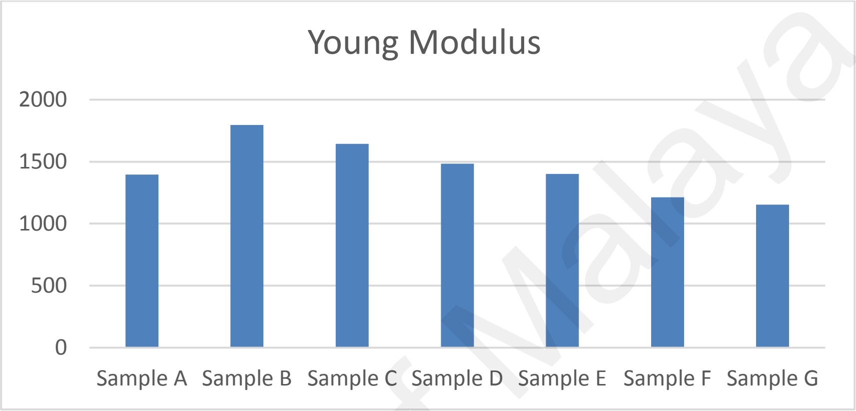

Figure 4.2: Trend chart of Young Modulus

According to Table 4.1 and Figure 4.2, the young modulus of starch / PLA blend shows a decreasing trend with the increase of starch content. The value of young modulus decreases from 1796.26MPa to 1483.31MPa by comparing the blend with starch content accounting for 3% with that accounting for 7%.

In the starch / PLA blend with 0.025g thrimethyl chlorosilane added respectively, the trend of young modulus still decreases with the increase of starch content. In the presence of thrimethyl chlorosilane, the value of young modulus decreases from 1399.77MPa to1153.76MPa by comparing the blend with starch content accounting for 3% with that accounting for 7%.

Therefore, by comparing the starch / PLA blend of same content, the addition of thrimethyl chlorosilane decreases the value of young modulus.

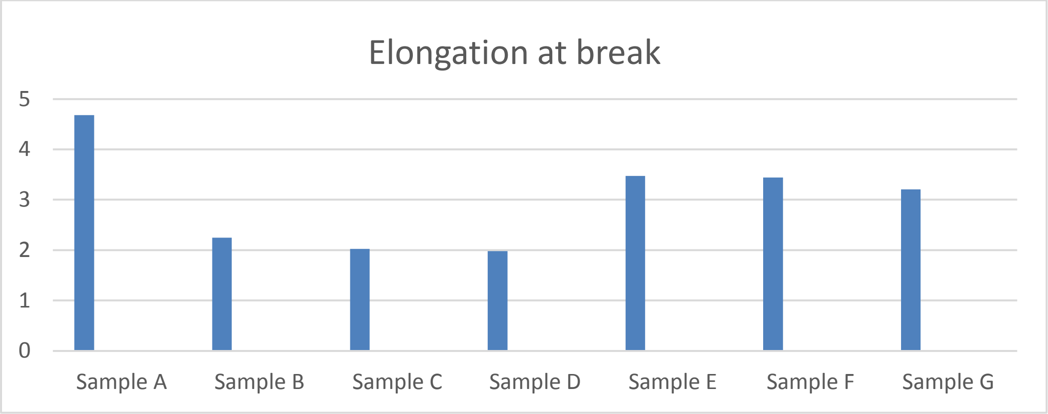

Figure 4.3: Trend chart of elongation at break

According to Table 4.1 and Figure 4.3, the elongation at break of starch / PLA (from sample B to sample D) blend showed a decreasing trend with the increase of starch content. The value of elongation at break decreases from 2.2453% to 1.98165% by comparing the blend with starch content accounting for 3% with that accounting for 7%.

In the starch / PLA blend with 0.025g thrimethyl chlorosilane added respectively, the trend of elongation at break still decreases with the increase of starch content. In the presence of thrimethyl chlorosilane, the value of elongation at break decreases from 3.47105% to 3.20743% by comparing the blend with starch content accounting for 3% with that accounting for 7%.

Therefore, by comparing the starch / PLA blend of same content, the addition of thrimethyl chlorosilane increases the value of elongation at break.

Hydroxyl groups have the strong interaction in starch molecule, with a high degree of crystallinity, the addition of starch reduces the flexibility of polylactic acid chain, making the movement of molecular chain difficult. At the macro level, the toughness of the blend material decreases, which reduces the elongation of fracture. Therefore, with the increase of starch content, the mechanical properties of the composites decreases (tensile strength, young modulus and elongation at break all decrease). Because PLA is a very brittle material, filling of PLA with native starch The seemingly unrealistic, as the brittleness is increased by the dispersed starch granules. While after TMCS addition, the elongation at break of PLA/ starch blend material increase. It was indicated that the addition of TMCS increased the compatibility between starch and PLA and improved the toughness of the blend material.

4.2 Spectrophotometer Analysis

Methylene blue is used as adsorbent and simulated as the pollutant. The adsorption capacity of the blend on methylene blue is measured. In this experiment, the absorption peak at the 665nm wavelength is chosen as the standard.

Studies the photocatalytic degradation of titanium dioxide by testing methylene blue (Methylene blue), choose methylene blue as an experimental pollutant (Lachheb et al., 2002). For instance, the absorption spectra of methylene blue shown in Figure 4.4 have three obvious absorption peaks at the wavelength of 665nm, 292nm and 246nm respectively and 665nm is the maximum absorption peak. Therefore, most of the literature adopts the peak (665nm) to quantitatively analyze the concentration of methylene blue to measure whether methylene blue is degraded or absorbed.

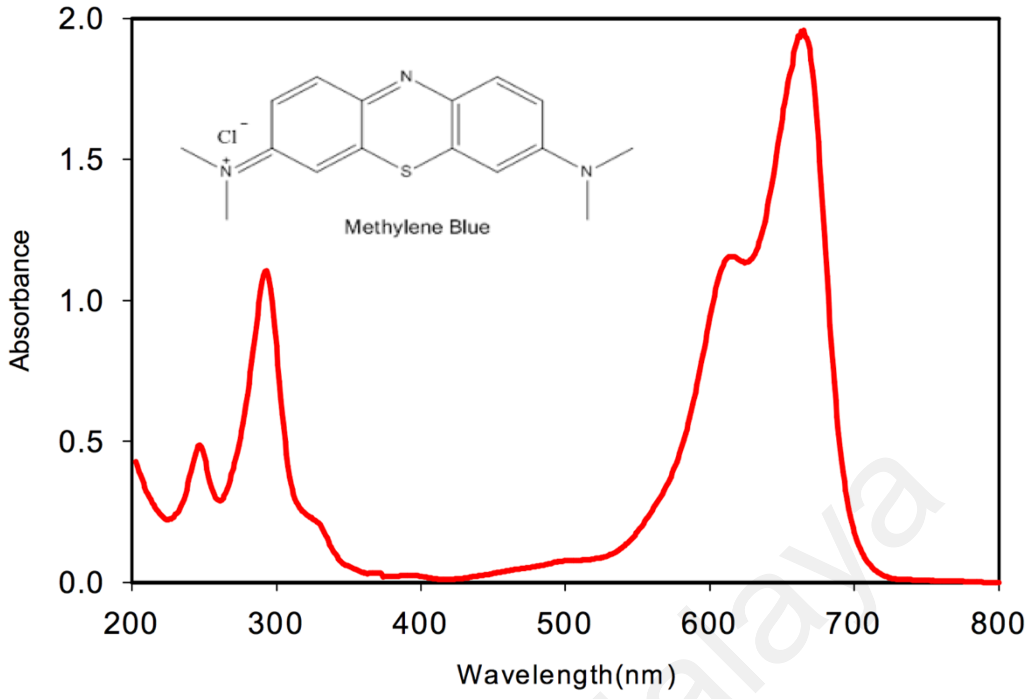

Figure 4.4: The absorption spectrum of methylene

The standard solution of methylene blue methanol is respectively configured and the concentration is 0.4ppm, 0.8ppm, 1.2ppm, 1.6ppm, 2.0ppm and 2.4ppm respectively. Through the UV-Vis spectrometer, the measured values are shown in table 4.2 and the relationship between absorbance and concentration is plotted.

Table 4.2 The absorbance of methylene blue standard solution of various concentrations at the 665nm wave length

Concentration	WL665.0
0	-0.00603
0.4ppm	0.008357
0.8ppm	0.018769
1.2ppm	0.068911
1.6ppm	0.102476
2ppm	0.144261
2.4ppm	0.203719

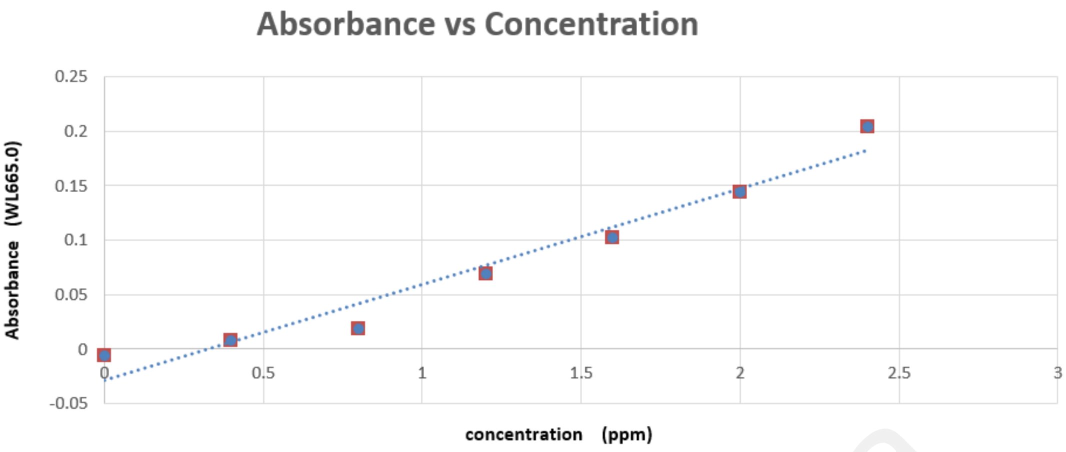

Figure 4.5: The relational graph of absorbance （665nm）and concentration of blue methanol

There are totally 7 samples of the composite materials made through fusing, blending and hot-pressing PLA / starch / thrimethyl chlorosilane of different proportions. All the samples are cut into the same size and immersed in 2ppm methylene blue standard solution. After 24hours, UV-Vis is used to detect as Figure 4.6 and 4.7. X line is the Methylene blue absorption spectrum of blank test.

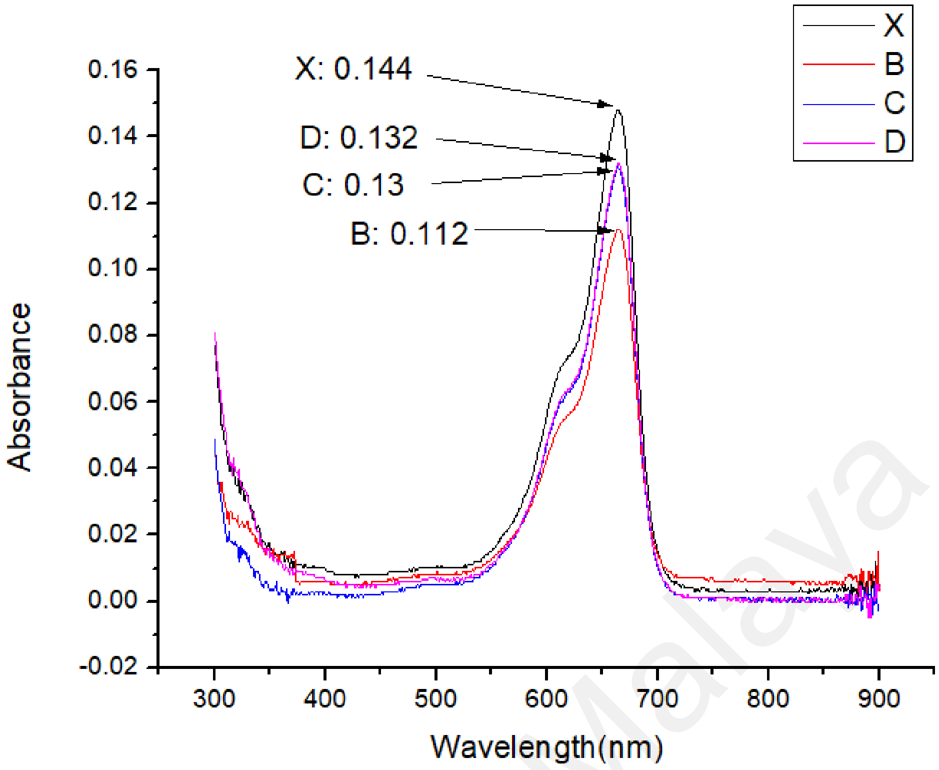

Figure 4.6: The solution absorption spectrum of starch / PLA blend immersed in 2ppm methylene blue solution for 24 hours

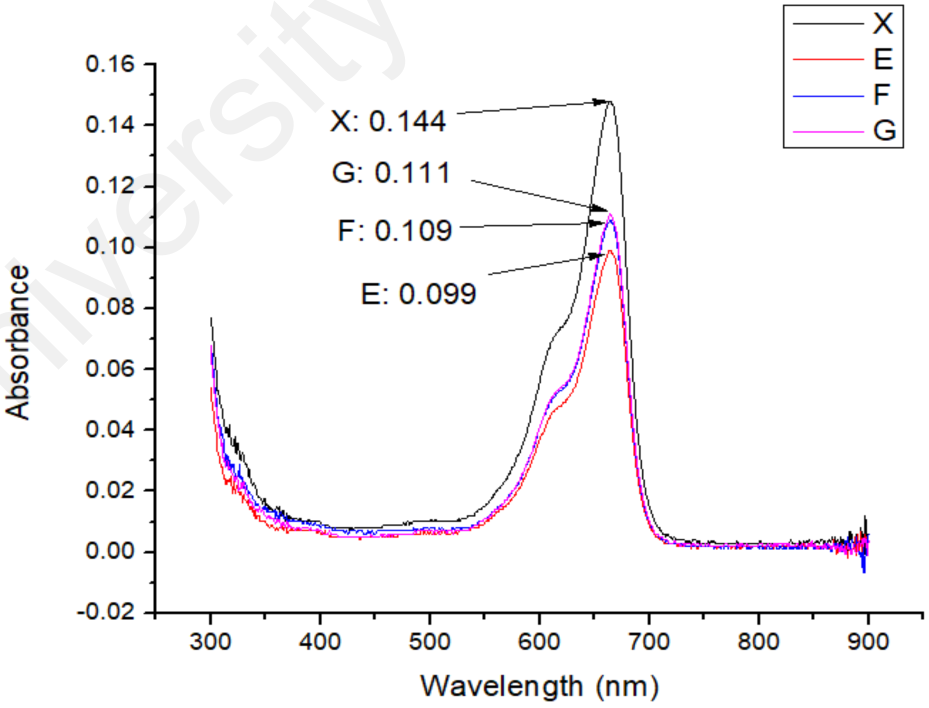

Figure 4.7: The solution absorption spectrum of starch / PLA blend immersed in 2ppm methylene blue solution after adding thrimethyl chlorosilane for 24 hours

Table 4.3 The absorbance of the residual solution at the 665nm wave length after the sample absorbs the methyl blue solution

Sample	Sample Type	WL665.0	Solution Concentration after the Absorption（ppm）
A	PLA 100%	0.117	1.67
B	PLA 97% + STARCH 3%	0.112	1.62
C	PLA 95% + STARCH 5%	0.13	1.8
D	PLA 93% + STARCH 7%	0.132	1.82
E	PLA 97% + STARCH 3% + TMCS 0.025g	0.099	1.49
F	PLA 95% + STARCH 5% + TMCS 0.025g	0.109	1.59
G	PLA 93% + STARCH 7% + TMCS 0.025g	0.111	1.61

Table 4.3 can pinpoint the absorption capacity. With the increase of starch content, the adsorption capacity of starch / PLA blend decreases. When thrimethyl chlorosilane is added, the adsorption capacity decreases with the increase of starch. Compared with the starch / PLA blend of same amount, the addition of thrimethyl chlorosilane increases the adsorption capacity.

Pure starch has adsorption. When the content of pure starch increases, the adsorption of starch to methylene blue should also increase. However, as the starch increased in the blend, the adsorption capacity decreased. Therefore, it can be determined that the adsorption of blends in this experiment is not purely physical adsorption. However, in the blend, which groups have a certain effect on the adsorption of methylene blue is a new problem, it is also the research direction of new water treatment chemicals.

4.3 FTIR Molecular Analysis

Figure 4.8 illustrates typical FTIR spectra of PLA, starch, and PLA/starch specimens. Four characteristic absorption bands centered at 1750, 2950, 2995 and 3510 cm^{-1}, corresponding to the motions of C=O bending, C-H aliphatic stretching, C-H aliphatic stretching (doublet) and C-O-O-H stretching vibrations, respectively, were found in the spectrum of PLA.

The FTIR spectra of PLA/starch specimens, are very similar to those of PLA; the four main absorption bands centered at 1750, 2950, 2995 and 3510 cm^{-1} were also found in the spectra of PLA/starch specimens. The absorption bands around 3000 to 3670 cm^{-1} were the O-H stretching vibration of starch.

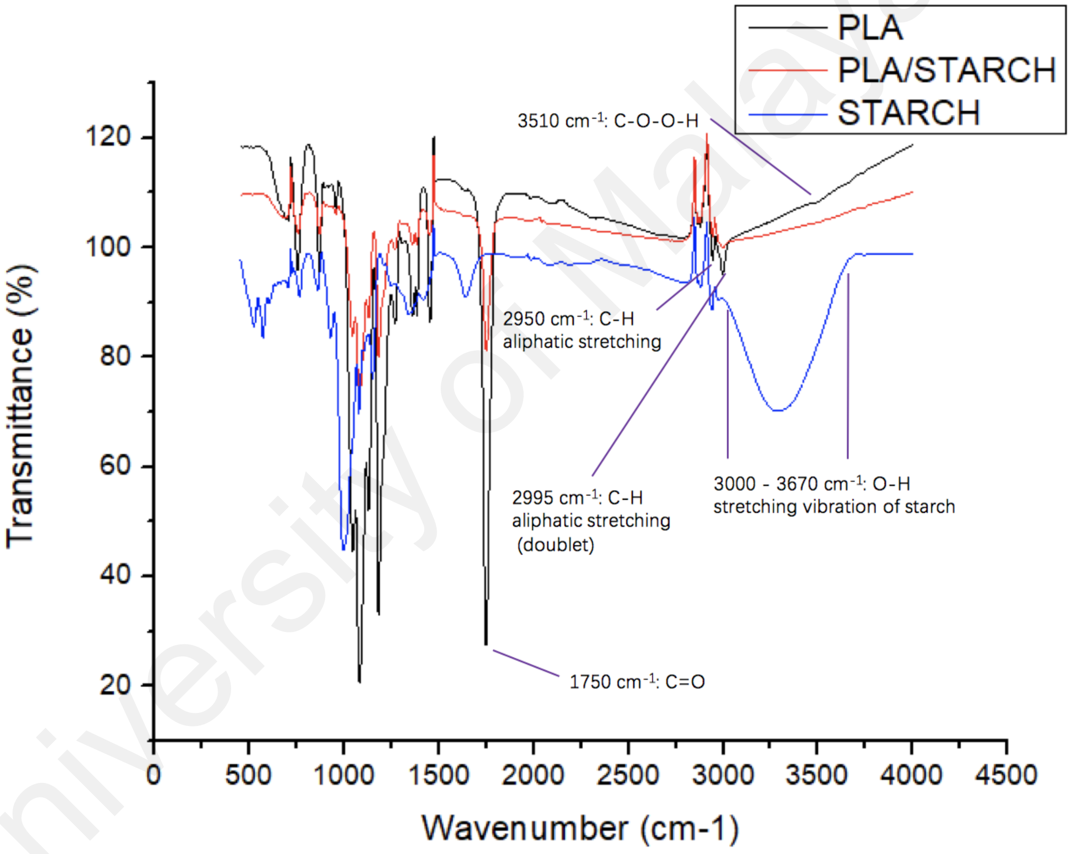

Figure 4.8: FTIR of: PLA、STARCH and PLA/STARCH

Figure 4.9 illustrates typical FTIR spectra of PLA/starch and PLA/Starch/TMCS specimens.

The FTIR spectra of PLA/starch specimens are very similar to those of PLA/Starch/TMCS.

Four characteristic absorption bands centered at 1750, 2950, 2995 and 3510 cm^{-1}, corresponding to the motions of C=O bending, C-H aliphatic stretching, C-H aliphatic stretching (doublet) and C-O-O-H stretching vibrations, respectively, were found in the spectrum of PLA/Starch/TMCS, but the obvious change of the above four main absorption bands explains that addition of small amount of TMCS don't change the major property of PLA/starch, but only have little influence.

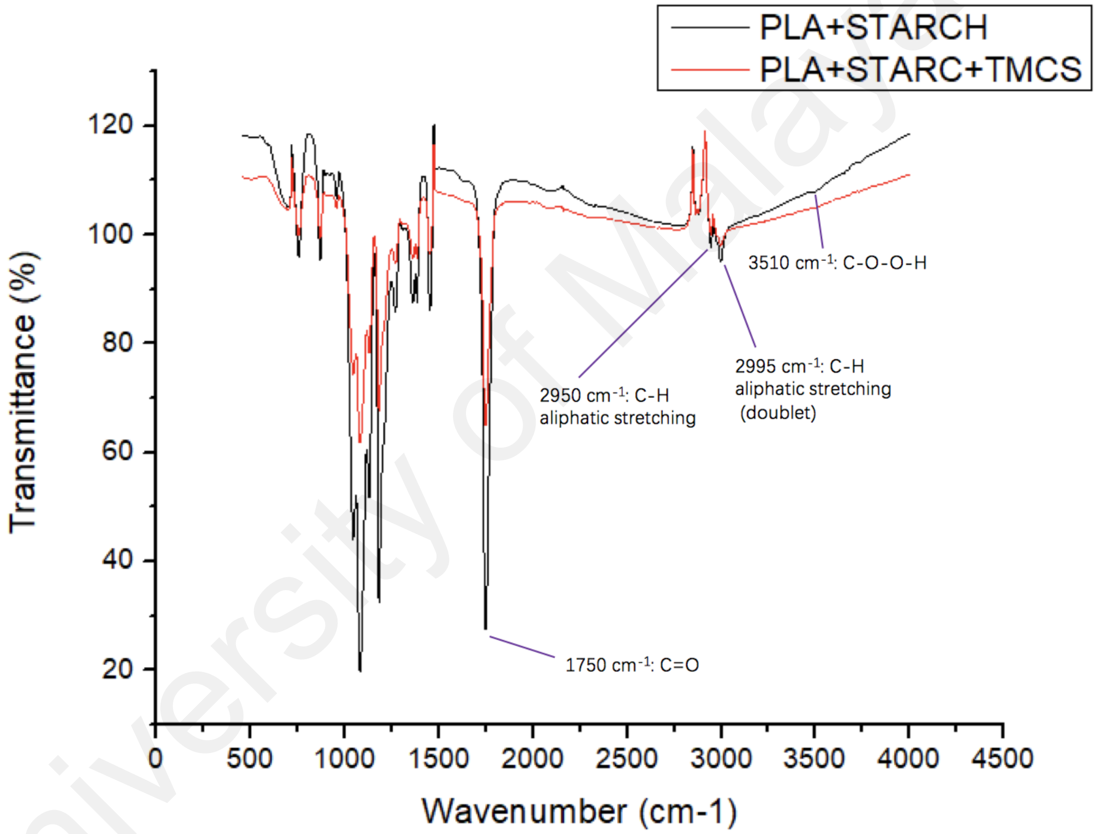

Figure 4.9: FTIR of: PLA/STARCH and PLA/STARCH/TMCS

4.4 Water Absorption Test

There are totally 7 samples of the composite materials made through fusing, blending and hot-pressing PLA / starch / TMCS of different proportions. Each sample is tested three times and the average value is taken. The weighing results of the sample water absorption test are as follows in Table 4.4

Table 4.4: Weighing results of sample water absorption test

Sample	Content of the Sample	Weight	Expansion Weight	Percentage Increase
A	PLA 100%	1.4823	1.486	0.25%
B	PLA 97% + STARCH 3%	1.5754	1.5808	0.34%
C	PLA 95% + STARCH 5%	1.2792	1.2848	0.44%
D	PLA 93% + STARCH 7%	1.5005	1.508	0.50%
E	PLA 97% + STARCH 3% + crosslink 0.025g	1.5676	1.5727	0.33%
F	PLA 95% + STARCH 5% + crosslink 0.025g	1.5262	1.5327	0.43%
G	PLA 93% + STARCH 7% + crosslink 0.025g	1.3374	1.3446	0.54%

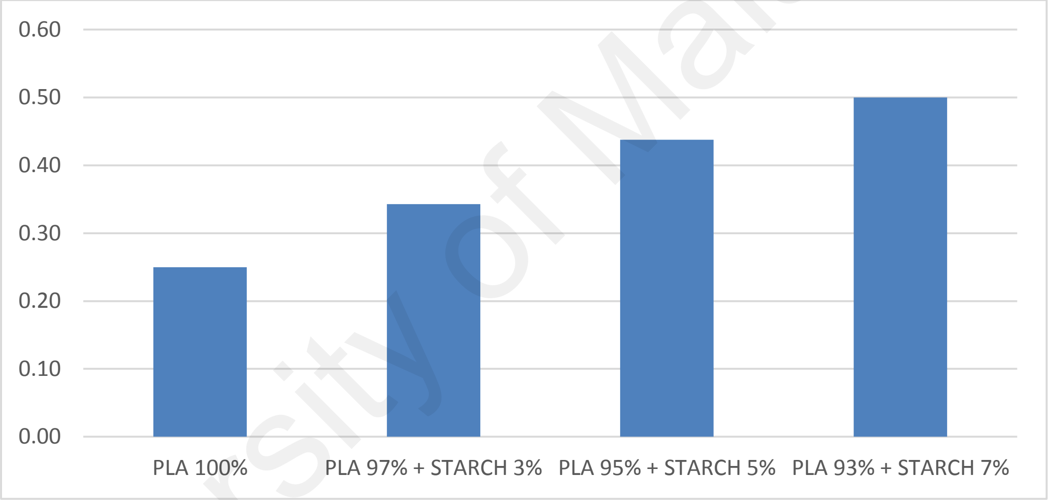

Figure 4.10: The Tendency chart of water absorption Test of Starch/PLA Blend

From Figure 4.10, it can be found that with the increase of the starch content, water absorption of starch/PLA Blend rises. The starch content increases from 3% to 7% and water absorption increases by 0.16%（24h）.

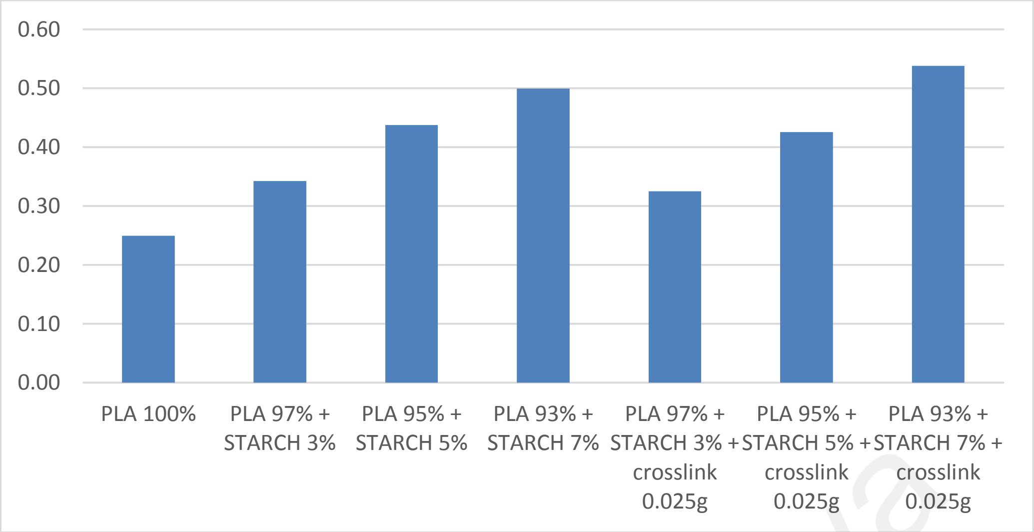

Figure 4.11: The Tendency chart of water absorption Test of Starch/PLA/TMCS Blend

From Figure 4.11, it can be found that the addition of a small amount of trimethylchlorosilane can hardly change water absorption of PLA / Starch Composites. With the increase of starch content, water absorption still maintains an upward trend.

The hydroxyl group in the starch is hydrophilic, and as the content of the starch increases, the hydroxyl group in the blend（PLA / Starch） also increases, so the water absorption also increases. When a small amount of TMCS is added and the content of the hydrophilic group in the blend （PLA / Starch） is not changed, the water absorption is hardly changed.

CHAPTER 5: CONCLUSIONS

This paper analyzes the experiments of the blends with different ratio of PLA, starch and trimethylchlorosilane by using the methods of measuring mixers and hot press machine. In the experiment, the mechanical properties, optical analysis and water absorption tests are conducted respectively. The changing trend of various properties of polylactic acid and starch at different mass ratios is analyzed as well as the influence of addition of trimethylchlorosilane on the properties of the composite. The final conclusions are as follow:

i. In the blend of PLA and starch, with the increase of starch content, the mechanical properties of the composites decreases (Tensile Strength, Young Modulus and Elongation at break all decrease), the absorbability decreases and the water absorption increases. With the addition of small amount of trimethylchlorosilaneby, the mechanical property of blends decrease. In comparison with the blends of PLA/starch with content, the addition of trimethylchlorosilaneby decreases Tensile Strength and young modulus while increase elongation at break and absorbability. However, it affects little about water absorbing quality. The FTIR analysis shows that the addition of trimethylchlorosilane does not substantially change the composition and structure of the blend system of starch / polylactic acid. The changes only occurred on several peak absorptions, which also leads to the changes in mechanical properties, adsorbability and absorbency.

ii. In the adsorption test of the blend with methylene blue, the blend adsorbed methylene blue. So, Starch/PLA/TMCS blends have adsorptive properties and can be further studied in the field of wastewater industry.

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