

**TENSILE PROPERTIES AND WATER  
ABSORPTION OF MINERAL FILLERS FILLED  
POLYLACTIC ACID COMPOSITES**

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**UNIVERSITI SAINS MALAYSIA**

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FILLERS FILLED POLYLACTIC ACID COMPOSITES**

By

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## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Tensile Properties and Water Absorption of Mineral Fillers Filled Polylactic Acid Composites”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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## LIST OF SYMBOLS

wt %	Percentage of weight
MPa	Megapascal
$\mu\text{m}$	Micro-meter
rpm	Revolution per minute
$\varepsilon$	Yield strain
$\sigma$	Yield stress
E	Young's Modulus
$E_b$	Elongation at break

## LIST OF ABBREVIATIONS

PLA	Poly (lactic acid)
PCL	Polycaprolactone
PBS	Poly (butylene succinate)
PE	Polyethylene
PS	Polystyrene
PVC	Poly (vinyl chloride)
PHA	Poly-hydroxyalkanoates
PEG	Polyethylene glycol (PEG)
ATEC	Acetyl triethyl citrate
TBC	Tributyl citrate
ATBC	Acetyl tributyl citrate
SEM	Scanning Electron Microscope
PSA	Particle Size Analyser
TS	Tensile Strength
YM	Young's Modulus

## **LIST OF APPENDICES**

- Appendix A      Tensile and Impact test for PLA/PEG
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# **SIFAT PENYERAPAN AIR DAN TEGANGAN KOMPOSIT POLILAKTIK ASID TERISI PENGISI MINERAL**

## **ABSTRAK**

Penambahan bahan mineral ke dalam biodegradasi polimer telah dikaji untuk mengenal pasti sifat bahan komposit. Kajian ini bertujuan untuk mengenal pasti kandungan optimum dalam komposit asid polilaktik (PLA). Sifat kerapuhan PLA menyebabkan ia perlu diaduk dengan polietilen glikol (PEG). Kesan penggunaan (PEG) disiasat menggunakan tiga kandungan PEG yang berbeza. Pengisi mineral telah dicirikan menggunakan penganalisis saiz zarah (PSA) dan pengimbas mikroskop electron (SEM) untuk mengkaji taburan saiz, bentuk dan saiz zarah. Penggunaan mesin skru berkembar ekstruder digunakan untuk mencampur adunan bahan mineral bersama PLA/PEG. Mesin suntikan acuan diguna untuk membentuk sampel ujian mengikut piawai ASTM D638. Sifat ketegangan seperti kekuatan, pemanjangan semasa putus, dan modulus Young diperolehi untuk komposisi komposit dengan pengisi mineral yang berbeza. Ujian penyerapan air dijalankan untuk melihat kadar penyerapan air dalam bahan komposit dan dibandingkan dengan PLA/PEG. Sifat tegangan menunjukkan bahawa PLA/PEG 15 % merupakan formulasi yang terbaik dengan pemanjangan takat putus dan kesan kekuatan yang tinggi. 30 wt % talkum dan siltech G500 merupakan pengisi mineral terbaik apabila diadukkan bersama PLA/PEG. Hasil menunjukkan kekuatan tegangan dan pemanjangan takat putus berkurangan dengan penambahan pengisi serta modulus Young meningkat. Keputusan kadar serapan air menunjukkan bahawa, PLA/PEG tanpa sebarang pengisi mempunyai kadar serapan air yang lebih rendah jika dibandingkan dengan pengisi mineral terisi PLA/PEG. Oleh itu, pengisi terbaik dalam komposit PLA/PEG ialah talkum 30 wt %.

# **TENSILE PROPERTIES AND WATER ABSORPTION OF MINERAL FILLERS FILLED POLYLACTIC ACID COMPOSITES**

## **ABSTRACT**

Addition of mineral fillers into the biodegradable polymer has been studied to identify the properties of composite materials. The study is aimed to identify the optimum loadings of different types of mineral fillers (talc, siltech G500, and Siltech G501) in polylactic acid (PLA). Due to the brittle properties of PLA, polyethylene glycol plasticizer (PEG) was blended with PLA. The effects of plasticizer were investigated using three different PEG loadings. Mineral fillers were characterized using particle size analyser (PSA) and scanning electron microscope to identify the particle size distribution, shape, and size of the particles. Mineral fillers filled PLA/PEG blends were mixed using twin-screw extruder. Injection moulding were used to fabricate the test sample according to the standard ASTM D638. Tensile properties such as tensile strength, elongation at break, and Young's modulus were obtained for different composition of mineral filled PLA composites. Water absorption test was done to investigate the rate of water absorption in composite materials in comparison with PLA/PEG. Tensile properties indicated that PLA/PEG 15 % is the best formulation exhibits higher in elongation at break and impact strength. For mineral fillers filled PLA/PEG, the best fillers are 30 wt % of Talc and Siltech G500. Results showed that the tensile strength and elongation at break trend decreased with addition of fillers and Young's modulus increased. Water absorption rate results showed that, PLA/PEG without any fillers having lower water absorption rate if compared with the mineral fillers filled in PLA/PEG. Thus, the best fillers in PLA/PEG composites is 30 wt % talc.

# CHAPTER 1

## INTRODUCTION

### 1.1 Overview

Biodegradable polymers are materials that has designed to decay naturally as a result of the action of living organisms following disposal. Biodegradable polymer is a polymer that were consider in bioactive environments degrade by the enzymatic action of microorganisms (e.g., bacteria, fungi, and algae). Chemical hydrolysis is one of nonenzymatic process that can disintegrate down the polymer chains. These biodegradable polymers are frequently produced by the process of plant CO<sub>2</sub> processing, they are degraded into CO<sub>2</sub>, CH<sub>4</sub>, water, biomass, humic matter, and other natural components during the process of biodegradation

Since petroleum – based polymers are still utilized in composite synthesis, the depletion of petroleum supplies and worries about environmental damage have resulted in a greater interest in biodegradable and renewable resources such as starch, cellulose, and natural products. Polylactide (PLA) is a potential biopolymer that has a high strength and modulus, a high degree of transparency, and exceptional thermal flexibility which making it a suitable thermoplastic for injection moulding, blow moulding, single – screw or twin – screw extrusion. As a result, the biodegradability of PLA along with its great characteristic, thus make it more viable alternative for applications with short lifecycles for example packaging and electronics.

Despite the facts, PLA shows some disadvantages. Their high-cost material in comparison to polymers such as polyethylene (PE) or polypropylene (PP), as well as PLA great in flammability, limit their utilization or application. As a result, the addition of fillers or plasticizer helps to adjust the mechanical characteristics therefore increase



resistance while keeping the cost low. Low molecular weight of PLA initially confined its applicability to biomedical sectors, even though the development of novel polymerization processes now allows the manufacturing of high molecular weight PLA that varies in applications such as packaging. Lactic acid that created by chemical synthesis or carbohydrate fermentation acts as primary building component of PLA.

For improvement in the mechanical properties of PLA, addition of fillers is needed. Fillers could improve the properties of impact because it may change the fracture mechanism from a straight line to one that is more complicated. This means the fracture profile will become longer (Picard et al., 2019). The presence of organic/inorganic fillers and their uniform dispersion within the polymer may contribute to increased toughness by absorbing energy and transferring it to the nearby particles, which is not achievable with neat polymers (De Campos et al., 2019). Previous works have been done to investigate the addition of mineral fillers such as talc to increase the stiffness and impact strength, and thermal conductivity. The toughened PLA/talc were investigated by Akbari et al., (2014). They combined epoxidized natural rubber and silane – treated talc. They have optimised the stiffness and impact strength of PLA by the ratio 60: 30: 10. Enhanced tensile and storage modulus of PLA were established in PLA/talc melt mixed and blown composites films due to strengthen capacity of talc particles. Others filler such as kaolin, calcium carbonate, and mica also act as main academic focusing on reinforcement of PLA.

Plasticizers used in a polymer processing to enhance the flow of the polymer melt, which ease to compound the polymer melt with reinforcing agents and fillers thus improve the flexibility of materials. Addition of plasticizer such as Poly(Ethylene Glycol) (PEG), TBC8 – eb (p-tert-butylcalix(8)arene ethylbenzene, Ehtylene-Bis-Streramide (EBS), and orotic acid will support higher crystallisation temperature but difficult to

measure the results due to several types of PLA used and high variance in crystallization property according to D – lactide content (Tábi et al., 2014). Some research introduced the PEG and talc shows synergistic effect for improvement of crystallization rate and produce high heat deflection tempered (HDT) in injections moulded PLA part for engineering utilization with affordable price (Li et al., 2007).

There are some properties for plastic packaging need to be consider which is the density, degree of polymerization, thermal properties for example glass transition temperature, melting temperature, and heat deformation temperature, chemical resistance, permeability, and morphological properties once designing the food packaging system. Plastics polymer can affect for the chemical composition, environmental, and physical states of raw materials. The advantages of plastics polymer provide in packaging which it become very light weight, low cost, and significant strength compared to the others packaging materials. Table 1.1 shows the changes of property in increasing crystallinity of plastic polymer packaging.

**Table 1.1** : Property changes occur during increases of crystallinity in plastic polymer packaging (Young et al.,2014)

Property	Value	
	Increased	Decreased
Physical property	Density	Permeability
	Opacity	Clarity
Thermal property	Heat sealing temperature	Heat sealing range
Mechanical property	Tensile strength	Compression strength
		Tear resistance
		Impact strength
		Toughness
		Ductility
		Ultimate elongation

## 1.2 Problem Statement

Usage of plastic packaging among the food and beverage industry often have adverse effects on the environment and become domestic waste due to rapid production of plastic products this has become motivation for this study. Most users are irresponsible, throwing their leftovers all over the place. If the waste is not properly disposed, it will remain in its original form for hundreds of years. Usually, the production of plastic packaging is made of synthetic polymers that cannot be degraded. It takes hundreds of years to decompose, and it is difficult to dispose naturally. Use of biodegradable polymer such as PLA as food container or packaging is one of solution. However, addition of cheap fillers such as mineral fillers will reduce the cost of the PLA raw materials. Despite that, the characteristic of PLA shows a brittle material. Thus, addition of plasticizer is significant to increase the crystallinity and reduce the brittleness of PLA.

Angela et al. (2008) studied the effects of inorganic fillers such as talc filled in PLA to improve the mechanical properties, the results show an addition of 2 wt % talc exhibits a strong nucleation effect on PLA properties. Huda et al. (2007) studied the mechanical characteristic of PLA / recycled newspaper cellulose fiber composites were greatly enhanced by compounding with 10 wt % talc. Meng et al. (2011) investigated the effect on mechanical properties of nano-clay / wood flour filled PLA exhibits great tensile properties at 30 wt % of wood flour.

Factors such as the amount of fillers, types of fillers, effects of plasticizer are important to be investigated in order to improve the properties of the PLA. Suggestion and recommendations to maintain or improve the production of biodegradable food packaging can be made with the aid of characterization results at the end of this study.

### **1.3 Research Objectives**

The objectives of this project are:

1. To determine suitable loadings of polyethylene glycol (PEG) as plasticizer (5, 10, and 15 wt %) based on tensile and impact properties of PLA/PEG.
2. To investigate the effect of different types of mineral fillers (talc, siltech G500, and siltech G501) with different weight fraction (15, 30, and 45 wt %) on the tensile properties of PLA/PEG.

## **1.4 Thesis Outline**

Chapter 1 discussed on the introduction of dissertation including background of biodegradable polymer, problem statement, and research objectives for this project.

Chapter 2 discussed on the literature review included the types of biodegradable polymer, formulation of biodegradable polymer composites, types of plasticizers, review on properties of mineral fillers filled PLA composites, and several types of compounding techniques.

Chapter 3 discussed about the raw materials have used and the methodology to conduct an experiment and characterization techniques for measurement results.

Chapter 4 discussed on the morphology of mineral fillers using scanning electron microscope and particle size analyzer were tabulated and observed based on the results. Mechanical properties of polymer composites were measured using tensile test and impact test and water absorption test were conducted to study the properties of mineral fillers filled PLA/PEG composites.

Chapter 5 discussed on the conclusion for research objectives and future suggestion.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Biodegradable Polymer

##### 2.1.1 Poly(lactic acid) or PLA

Poly(lactic) acid or PLA is one of biodegradable polymer materials that can degrade rapidly at temperatures well above ambient (room temperature), make it as excellent material. Moreover, poly (lactic acid) has four stereoisomeric forms because it is optically active. There is poly (L lactic acid) (PLLA), poly (D-lactic acid) (PDLA), poly (D, L-Lactic acid) (PDLLA), meso-poly (lactic acid) (MPLA). PLA is a biodegradable, aliphatic polyester made from renewable resources that were recently highlighted in research objectives to meet the specific need. Because of its transparency, high strength, and stiffness it outperforms many other biobased polymers on the market today. PLA has gaining popular because of their advantages of being able to alter properties to be suitable for specific applications by adding fillers. (Maharana et al., 2009).

However, PLA also has significant disadvantages, including a low melt strength, hardness, and service temperature; a slow crystallization rate, poor processability and brittleness (Jacobsen et al., 1999). Improvement in performance capabilities of PLA have been incorporated with fillers whether natural or synthetic polymer and can be utilize or particulate in nature.

Despite that, PLA is thermally unstable and loses molecular weight quickly when heated to processing temperatures. PLA's ester bonds breakdown after thermal processing or hydrolysis. PLA goes through thermal processing, but the deterioration occurs at temperatures below the melting point of the polymer. Consequently, at the melting point the rate of degradation rapidly increases. It has been proposed that heat

deterioration is the primary cause of random main – chain scissions. Several reactions, for example hydrolysis, depolymerization, oxidative degradation, and interand intramolecular trans-esterification processes to monomers. It has been proposed that oligomeric esters are involved in the degradation reactions during heat treatment (Okada et al., 2002).

PLA crystals can grow in three structural states known as  $\alpha$ ,  $\beta$ , and  $\gamma$  forms. They are distinguished by various helix conformations and cell symmetries that emerge as a result of thermal and/or mechanical treatments.  $\alpha$  form demonstrate a grows upon melt or cold crystallization,  $\beta$  form grows during mechanical stretching and more stable compared to  $\beta$ , while  $\gamma$  form used to develop on hexamethylbenzene substrate (Farah et al.,2016). Table 2.1 shows the different grades of PLA.

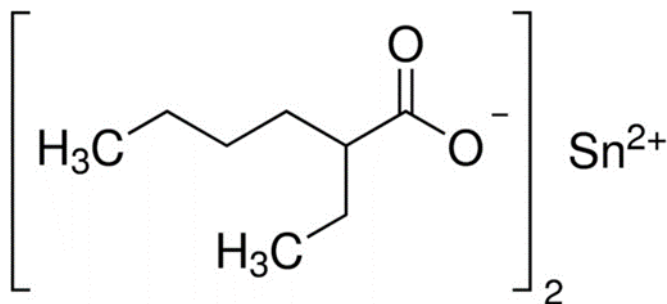
**Table 2.1** Properties of different grades of PLA (Miller et al., 2000)

<b>PLA Grade</b>	<b>Density (g / cm<sup>3</sup>)</b>	<b>T<sub>g</sub> (° C)</b>	<b>T<sub>m</sub> (° C)</b>	<b>Molecular weight, M<sub>r</sub> (g / mol)</b>	<b>Reference</b>
PLA 2003D	1.24	61	169	35.0 x 10 <sup>4</sup>	(Yang et al., 2013)
PLA 4043D	1.24	130	145 - 160	150 x 10 <sup>3</sup>	(Girdthep al., 2014)
PLA 4032D	1.24	150	160	253 x 10 <sup>3</sup>	(Shuo Qiu et al., 2020)

PLA can be synthesized with two different methods. First and the most common method used is the ring-opening polymerization (ROP). This is because high molecular weight of PLA can be produced by using this method. The mechanism involved in ROP can be ionic either is anionic or cationic or coordination-insertion, depending on the catalytic system. (Cama et al., 2017)

There are two common catalysts used in this polymerization method. They are aluminium and tin alkoxide. However, tin catalyst namely tin 2-ethylhexanoate, as shown

in Figure 2.1 has been widely used in PLA synthesis. This is because it is more hydrolytically stable than aluminium catalyst and easier to handle during polymerization process. It is frequently used as initiator and co-initiator in PLA homopolymer synthesis. (Plackett and Vázquez, 2004)



**Figure 2.1** : Chemical structure of Tin 2-ethylhexanoate (Cama et al., 2017).

Due to their low-cost material, the lactide ring – opening polymerization is the most commonly used techniques for producing high molecular weight PLA in the market. High molecular weight polylactide is normally used for implant devices, scaffold, and internal sutures. Nonetheless, new approaches enable more cost-effective manufacture for high molecular weight PLA. The neutral characteristic such as low toxicity has promising in reducing the waste disposal problems through use in food packaging and additional consumer items (Lim L et. al, 2009).

PLA's optimize qualities based on the number of enantiomers, indicating that molecular weight has no effect on the final properties of polymer. PLA is also widely recognized for having relatively good optical, mechanical, physical, and barrier qualities as compared to some petroleum polymers. The adaptability of PLA allows for the fulfilment of a wide variety of properties can be fulfilled, that is crucial since different kinds of requirements been shows on Table 2.2 below.



**Table 2.2** : Similarities on the properties between PLA and different petroleum – based polymers

<b>Properties</b>	<b>Petroleum – based polymers</b>	<b>References</b>
Permeability coefficients of CO <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub> and H <sub>2</sub> O	Lower than PS but higher than PET	(Auras RA et. al, 2005)
Barrier properties against ethyl acetate and d-limonene (organic permeants)	Similar to PET	(Harte B et. al, 2006)
Mechanical properties of oriented PLA	Higher than PS and similar to PET	(Auras RA et. al, 2005)
Flexural moduli and tensile	Higher than HDPE, PP and PS	(Dorgan JR et. al, 2000)
Elongation and impact strength	Lower than HDPE, PP and PS	(Dorgan JR et. al, 2009)

### 2.1.2 Poly(butylene succinate) or PBS

Poly(butylene succinate) or PBS is one of biodegradable polymers that were fabricated from petroleum based materials, often known as green polymeric matrices. PBS degrades more quickly in soil than petrochemical plastic and may be less hazardous to the environment. PBS has a melting point of 115 °C, which means it takes less time to melt or mix with other materials (Rafiqah et al., 2021). PBS was simplest to process and handle when combined with other materials. Because it is made from petroleum-based components, PBS has a higher rigidity but slightly fragile. PBS offers outstanding mechanical qualities as well as strong thermal stability. PBS's biodegradability is an appealing feature for single-use food packaging since it degrades at high rates in a short period of time. It is also designated as compostable by the biodegradable products institute and is available in direct food contact grades (Nazrin et al., 2020).

The structure of PBS is a versatile semi-crystalline polymer with a semi-crystalline structure. The characteristics of PBS has become demand in sectors of industry due to strong elongation properties and can be use in a number of applications. The chemical structure of PBS has an ester group that degrades into low molecular weight polymers when exposed to water. PBS has  $\alpha$  or  $\beta$  crystal polymorphs. The  $\beta$  structure can

be found when the material is under strain (Kanemura et al., 2012). Despite this, softness and gas barrier properties are lacking, requiring PBS to be blended with other materials such as fillers to satisfy application specification. PBS also provides a wide range of workability. The glass transition temperature should be lower than room temperature to allow for manufacturing methods such as extrusion, injection molding, and thermoforming. Table 2.3 shows the different properties of melting temperature ( $T_m$ ), glass transition temperature ( $T_g$ ), and grades of PBS.

**Table 2.3** Properties of different grades of PBS (Liu et al., 2009).

PBS Grade	MFI	Density (g/cm <sup>3</sup> )	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Reference
Molecular Weight 80,000	-	1.24	-44.3	109	27	-	(De Moraes Crizel et al., 2016)
Bionelle 1020 MD	20-34 g/10 min (at 140° C and 2.16 kg)	1.23	59.7	114.1	-	643	(Someya et al., 2004)
Bionelle 1020 MD	25 g/10 min at (190° C, 2.16 kg)	1.26	-32	115	33.7	707	(Ayu et al., 2020)
FZ91PM	5 g/10 min at (190° C, 2.16 kg)	1.26	78	115	20	450	(Zhang et al., 2012)
Bionelle	5 g/10 min at (150 °C, 2 kg)	1.26	-32	114	32	30	(Ren et al., 2003)

### 2.1.3 Polycaprolactone (PCL)

Polycaprolactone or PCL is an aliphatic polyester which has widely investigated as a biodegradable material, it demonstrates a low melting point (57 °C) and low glass – transition temperature (-62 °C). PCL can be degraded by microorganism as well as by a hydrolytic mechanism under physiological conditions. Under certain circumstances, it is possible to enzymatically degrade crosslinked PCL (termed enzymatic surface erosion). Low molecular-weight fragments of PCL are also reportedly absorbed by macrophages

intercellularly.  $\epsilon$ -caprolactone is a relatively cheap cyclic monomer (Hirami et al., 2009). A semi-crystalline linear polymer is obtained from ring-opening polymerization of  $\epsilon$ -caprolactone in presence of tin octoate catalyst.

PCL dissolves in a variety of solvents, because of the lower glass transition temperature that were range in  $-60$  °C and the melting point between  $60$  and  $65$  °C. At an ambient temperature (room temperature), PCL becomes a semi rigid material with a modulus between low- and high-density polyethylene, a tensile strength of  $23$  MPa and a high elongation to break a (more than  $700\%$ ). In polyurethane formulations, PCL is frequently used as a compatibilizer or a soft block. Moreover, PCL is easily biodegraded by enzymes and fungi. Table 2.4 demonstrate the characteristic of physical and chemical for PCL.

**Table 2.4:** Properties of physical and chemical of PCL (Vroman et al., 2009)

Property	Melting point (°C)	Tensile stress at break (MPa)	Elongation at break (%)	Tensile modulus (MPa)	Density (g / cm <sup>3</sup> )	Reference
PCL (Tone 787)	60	4	800 – 1000	386	1.145	(Gross et al., 2002)
PCL	59 to 64	4 to 28	700 – 1000	390 – 470	-	(Imran et al., 2010)

## 2.2 Thermoplastic Polymers

Thermoplastic polymers change their properties when heated and cooled. Thermoplastics become soft when heat is applied and on the other hand have a smooth, hard finish when cooled. Thermoplastic polymer has high molecular weight due to it is made up of long, unlinked polymer molecules. They rely on other interactions, such as dipole-dipole interactions, aromatic ring stacking, or Van der Waals forces because the molecular chains are unlinked (Kristoff, 2018). Below a particular temperature, thermoplastics typically develop a crystalline structure that gives them a flawless surface finish and great structural strength. Thermoplastics are elastic when the critical temperature is exceeded. Because thermoplastics can be melted and reused without affecting their physical characteristics as they are a recyclable polymer. The wastes are normally ground into chips, melted, refined to remove impurities, and reused as reclaimed material (Kristoff, 2018). Polyethylene (PE), Polypropylene (PP), Polyvinylchloride (PVC), Polystyrene (PS), Polytetrafluoroethylene (PTFE), also known as Teflon, and polyamide, often known as nylon, are the most frequently encountered thermoplastic polymers. Table 2.5 shows the recycling symbol and the properties of thermoplastic polymers.






PE is normally classified as low-density polyethylene (LDPE) and high-density polyethylene (HDPE). LDPE is used mainly in film applications due to its toughness, flexibility and relative transparency, making it popular for the applications where heat sealing is necessary. HDPE is the most widely used plastic for many types of bottles and containers. Unpigmented bottles are translucent, having good barrier properties and high stiffness, therefore it is well suited to packaging products with a short shelf life such as milk. Furthermore, HDPE is good in chemical resistance, therefore it also used for packaging many household and industrial chemicals such as detergents and bleach.

PP having a good chemical resistance and high melting point, about 160°C making it good for hot-fill liquids. PP also has an excellent optical clarity in biaxially oriented films and stretch blow molded containers. The low moisture vapour transmission and inertness toward acids, alkaline and most of the solvent making PP is suitable to be used in packaging application.

PS is a versatile plastic which can be rigid or foamed. General properties of PS are clear, hard and brittle. However, it has a relatively low melting point. PS is often combined with rubber to prepare high impact polystyrene (HIPS) which is used for packaging and durable applications where toughness is critical, but not clarity.

PVC has high impact strength, brilliant clarity and excellent processing performance. In addition, PVC has good grease, oil and chemical resistance, weatherability, flow characteristics and stable electrical properties. The vinyl products can be broadly divided into rigid and flexible materials.

**Table 2.5:** Recycling symbol and the properties of thermoplastic polymers (Attaran et al., 2017)

Thermoplastic Polymer	Recycling Symbol	Properties
HDPE		Stiff, strong, tough, resistance to chemical and moisture and easy process
PVC		Stiff, medium strong and transparent material, resistance to chemical, grease and oil, good flow characteristics and stable electrical properties
LDPE		Flexible, strong, tough, easy to seal, resistance to moisture
PP		Harder, denser, transparent and resistance to heat and chemicals
PS		Clear, hard and brittle material; foaming produces an opaque, rigid, lightweight material with impact protection and thermal insulation properties

## **2.3 Formulation of biodegradable polymer composites**

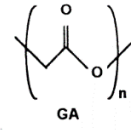
### **2.3.1 Biodegradable polymer**

Biodegradable polymers can be classified into synthetic and natural polymers. The term of “synthetic polymers” referring to polymers that have been synthesized artificially in laboratories. It is also well-known as man-made polymers. Synthetic polymers are manufactured from petroleum oil in a control environment and have a carbon-carbon backbone which hold the monomers together, forcing them to bond. Catalyst is used to initiate or accelerate the reactions between monomers. The example of synthetic polymers are polyethylene (PE), polystyrene (PS), polyamides (nylon), poly(vinyl chloride) (PVC), synthetic rubber, teflon, epoxy, and several others (Gross and Kalra, 1999).

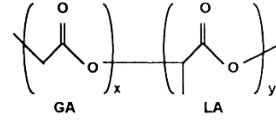
Synthetic polymers are a polymer that contain hydrolyzable backbone such as ester, amide, and urethane that include the addition of additive such as antioxidants. Figure 1.1 shown as the structure of polymers that contain hydrolyzable backbone. Majority of traditional polymers generated from petroleum resources are resistant to deterioration. Addition of additive will help to speed up biodegradation. The only steps for degrading polyolefins by introduce antioxidants into the polymer chains. Under ultra – violet light these antioxidants will react then cause photo – oxidation degradation. However, the biodegradability of this systems is still debatable. Synthetic polymer that commonly used as polymeric materials in a wide application was listed in Table 2.6 with several advantages and disadvantages.



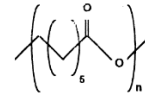
**Poly (glycolic acid) PGA**



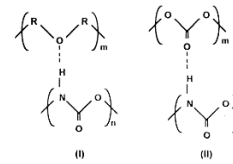
**Poly (glycolic acid – co – lactic acid) PGA/LA**



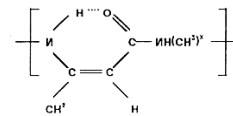
**Polycaprolactone PCL**



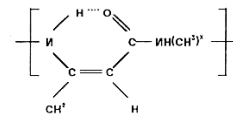
**Polyether – polyurethane (i)**



**Polyester – polyurethane (ii)**



**Poly (amide – enamine)s**



**Figure 2.2** : Polymer structure with hydrozable backbone (R. et. al,1998).

**Table 2.6:** Advantages and Disadvantages of Synthetic Biodegradable Polymers  
(Kunduru et al., 2016)

<b>Polymer</b>	<b>Advantages</b>	<b>Disadvantages</b>
<b>Poly lactides</b>	Highly processable polymers	Limited degradation with highly acidic degradation products
<b>Poly (ortho esters)</b>	Controllable and pH-sensitive degradation	Weak mechanical properties
<b>Polyphosphazenes</b>	Availability of Synthetic flexibility	Synthesis not direct forward
<b>Polyanhydrides</b>	Significant monomer flexibility	Low molecular weight of polymers and weakness in mechanical properties
<b>Polycaprolactone</b>	Highly processable polymer	Low rate of degradation
<b>Polyurethanes</b>	Strong mechanical polymers and good physical stress handle	Not often degrade and needed ester-urethane copolymerization
<b>Polycarbonates</b>	Dependent mechanical properties and surface eroding polymers	Limited degradation and copolymerization are required with other polymers

The advantages of biodegradable polymers such as mechanical behaviour are relay on their chemical composition, the production and storage, and characteristics of processing, the ageing and the conditions of application make them dominant in various application including plastic packaging and others. Several definitions for biodegradation plastic have introduced by authority's standards such as ISO 472, Proposal of ASTM subcommittee D20.96, Japanese Biodegradable Plastic Society, and DIN 103.2. ISO 472 defined a plastic that were intended to undergo a significant change in its chemical structure under specific environmental conditions, resulting in the loss of some properties that may vary as measured by standard test methods appropriate to the plastics and

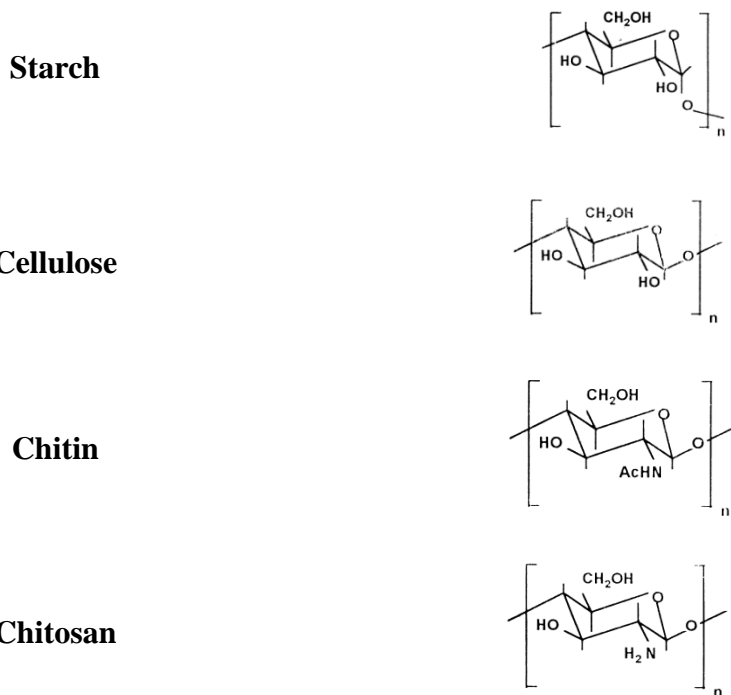
application over a time period that determines its classification. The chemical structure changes as a result of the action of naturally existing microbes.

Proposal of ASTM subcommittee D20.96 were described biodegradation as a plastic polymer that degrade or decompose due to bond scission in the backbone of polymer caused by chemical, biological, and physical processes in the environment. Japanese biodegradable plastic society explain on biodegradable plastic are polymeric polymers that degrade into lower molecular weight molecules, with at least one step occurring through metabolism in the presence of naturally existing organisms (Fakuda et al.,1992). DIN 103.2 was state the biodegradation of plastic substance is a process that results in naturally occurring metabolic end products.

Natural polymers are the polymers that were readymade by a nature on earth which extracted from plants or animals and no need to be observed on how they are synthesized. Conjugation, cross-linking, and chemical modification are made possible by the existence of reactive sites. Natural polymers are cheap and sometimes have biological effects on their own. This bioactivity can be bad because it can cause an immune reaction that's not good. The example of natural polymers is polysaccharides, polypeptides (e.g., silk, keratin, and hair), starch, cellulose, proteins, and poly-hydroxyalkanoates (PHA) (Kunduru et al. 2016). Natural polymers are inexpensive in cost and elicit the biological activity between themselves. Comparison between a natural polymer and synthetic polymer is illustrated in Table 2.7.

Polysaccharides, such as starch and cellulose are the most prominent family for these natural polymers. Proteins and other natural polymers can be utilized to create biodegradable products. Those would be the two most important renewable biopolymer sources. Natural polymers are frequently chemically introduced to increase their

mechanical characteristics or to change their rate of degradation. Figure 2.3 shows some of structures for polysaccharides.



**Figure 2.3 :** Structures for Polysaccharides (R. et. al, 1990).

Potatoes, corn, wheat, and rice are the most common sources of starch. Starch were produced of amylose (poly – 1,4 – D – glucopyranoside), a linear and crystalline polymer and amylopectine (poly – 1,4 – D – glucopyranoside), a branching and amorphous polymer. The relative quantities and molar masses of amylose and amylopectine varies depending on the starch source, resulting in materials with varying mechanical characteristics and biodegradability (Aman et. al, 1998). As the amylose concentration of starch increases, the elongation and strength also increase. Starch also known as hydrocolloid biopolymer, which the low-cost polysaccharide and it is abundantly available then the cheapest for biodegradable polymers. Enzymes hydrolyze the acetal bond to degrade starch. Amylases will attack the  $\alpha$  - 1,4 link whereas

glucosidases attack the  $\alpha$  - 1,6 link. Thus, it makes the degradation products are not harmful and non – toxicity (Yukuta et. al, 1990).

Cellulose also known as polysaccharide that made of plants, it is a linear polymer called cellobiose with exceptionally long macromolecular chains. Cellulose is crystalline, insoluble in all organic solvents, and insoluble in water (Chandra et. al, 1998). The biodegradation of cellulose occurs by enzymatic oxidation with peroxidase secreted with fungus. They also can be degraded by bacteria and cellulose is consider a product of starch deterioration are non – toxic. Cellulose esters are polysaccharides that have been changes. Various degrees of substitution are possible. Their mechanical characteristics and biodegradability deteriorate as the degree of replacement rises (Isabelle et. al, 2009).

**Table 2.7:** Comparison between a natural polymer and synthetic polymer (Kundururu et al., 2016)

<b>Natural Polymer</b>	<b>Synthetic Polymer</b>
Naturally occur	Produce from artificial
Natural reactions control the properties	Controlling the reaction can determine high engineered properties
Biodegradable	Some synthetic polymers are biodegradable
The chains length of molecules is similar	Chain length depends by the reaction conditions
Carbon, oxygen, and nitrogen are common backbone	Carbon backbone

### 2.3.2 Plasticizer

Plasticizers are often used in polymer processing to enhance the flow of the polymer melt, make it easier to compound the polymer melt with reinforcing agents and fillers, and improve the final material's flexibility plasticizers used in a variety of applications, but not limited to triethyl citrate (TEC), acetyl triethyl citrate (ATEC), tributyl citrate (TBC), acetyl tributyl citrate (ATBC), and polyethylene glycol (PEG). Plasticizers have been widely implemented to enhance glassy polymer processibility, flexibility, and impact toughness, as well as to reduce the glass transition temperature ( $T_g$ ) (Mascia et al., 1992).

PEG is a crystallizable, thermoplastic polyether typically ending with hydroxyl groups that is formed by anionic ring opening polymerization of ethylene oxide and is one of the most effective PLA plasticizers. It has great mobility, nontoxicity, and excellent biocompatibility, hydrophilicity, lubricity, bond ability and dispersibility. Furthermore, PEG is soluble in water and many organic solvents. Because of the benefits listed above, PEG has been widely employed in pharmaceutical and biomedical disciplines, cosmetics, the chemical industry, and food processing (Wang et al., 2015).

PEG has very strong miscibility with PLA because the terminal hydroxyl groups in PEG molecules can react with the carboxyl groups in PLA molecules. The addition of the appropriate amount of PEG can not only increase the hydrophilicity, flexibility, and impact toughness of PLA, but also the degradation rate and crystallisation kinetics of PLA. Meanwhile, the integration of PEG can still maintain PLA's biodegradability, biocompatibility, and food-contact status due to PEG's biodegradability, biocompatibility, and nontoxicity. As a result of the above investigation, PEG is a good plasticizer for PLA and can considerably improve the mobility of PLA molecular chains as well as the strain at break of PLA.

Sheth et al., (1997) investigated the effect of PEG content on the miscibility and mechanical properties of PLA/PEG blends by melt-blending PLA and PEG ( $M_w 2.0 \times 10^4$ ) in weight ratios of 100/0, 90/10, 70/30, 50/50, and 30/70. They discovered that the compatibility of PLA/PEG varied from full miscibility to partial miscibility depending on the PEG concentration. Tensile strength and modulus of the PLA/PEG blends declined below 50% PEG content, although elongation rose. However, over 50 wt percent PEG, the mix crystallinity increased significantly, resulting in a rise in tensile modulus and an apparent drop in elongation at break.

Furthermore, they discovered that both PLA and PEG in the blends could crystallise, and the presence of PEG aided PLA spherulite development. Furthermore, Baiardo et al. (2003) used PEGs with varying molecular weights ( $M_w 400 - 10,000$ ) and acetyl tri-n-butyl citrate (ATBC) to plasticize PLA. They discovered that both PEG and ATBC successfully decreased the  $T_g$  of PLA. PEG miscibility limit in PLA rose with decreasing molecular weight (15 wt % for PEG 10,000, 30 wt % for PEG 400), whereas ATBC miscibility limit was 50 wt %. The plasticizing effectiveness of PEG decreased as its molecular weight increased (Sheth et al., 1997).

### **2.3.3 Mineral Fillers**

Mineral fillers are commonly used in the plastics industry to increase qualities, particularly stiffness, and reduce the quantity of plastics used, resulting in lower material prices. Because of their stiffness and heat resistance, talc and asbestos fibers were the first commercially utilised fillers for polypropylene (Jancar et al., 1999). Other fillers provide very different purposes. For example, barium sulphate improves sound absorption, wollastonite improves scratch resistance, solid glass spheres enhance dimensional stability and hardness, hollow glass spheres reduce density, and combinations of glass