TENSILE AND IMPACT PROPERTIES OF MINERAL FILLERS FILLED POLY(LACTIDE) ACID COMPOSITES

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TENSILE AND IMPACT PROPERTIES OF MINERAL FILLERS FILLED POLY(LACTIDE) ACID COMPOSITES

by

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LIST OF SYMBOLS

°C	Degree Celcius
wt%	Weight Percentage
T_g	Glass Transition Temperature
g/cm^3	Density per centimeter cubic
MPa	Megapascal
D_{50}	Mass median diameter

LIST OF ABBREVIATIONS

$CaCO_3$	Calcium Carbonate
NS	Nepheline Syenite
PLA	Polylactide Acid
PEG	Polyethylene Glycol
SEM	Scanning Electron Microscope

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SIFAT-SIFAT TEGANGAN DAN IMPAK KOMPOSIT POLI(LAKTIK) ASID TERISI PENGISIAN MINERAL

ABSTRAK

Penggunaan bahan polimer dalam bidang pembungkusan makanan telah dikekalkan sejak beberapa dekad yang lalu sehingga kini. Polimer terbiodegradasi telah disiasat untuk menggantikan polimer petrokimia asal kerana kemesraan terhadap alam sekitar. Asid Polilaktida adalah salah satu polimer terbiodegradasi biasa yang telah disiasat untuk penggunaan bahan pembungkus makanan. Tetapi PLA mengandungi kelemahan pada sifat mekanikal yang mempengaruhi penggunaannya. Tujuan penyelidikan ini adalah untuk mengkaji kesan pembebanan berbeza Polietilena Glikol (PEG) dan pengisi mineral (Kalsium Karbonat, Nepheline Syenite dan Sibelite) terhadap sifat mekanikal PLA. Fabrikasi komposit dilakukan dengan mengeringkan bahan dalam 50 ℃ dan dicampur cair dengan penyemperit skru berkembar. Bahan yang dihasilkan adalah membentuk bentuk dengan menggunakan acuan suntikan dan penekan panas untuk membentuk bentuk bagi ujian tegangan dan ujian impak. Zarah pengisi mineral dicirikan oleh Penganalisis Saiz Zarah (PSA) dan Mikroskop Elektron Pengimbasan (SEM). Hasil kajian menunjukkan bahawa penambahan Kalsium Karbonat menyebabkan peningkatan sifat tegangan daripada 15wt% kepada 45wt% mencapai maksimum pada 36.47 MPa manakala penambahan dua pengisi lain menyebabkan berkurangan dengan peningkatan beban pengisi yang mencapai 18.08 MPa (Nepheline Syenite) dan 17.71 MPa (Sibelit). Pemanjangan semasa putus berkurangan bagi ketiga-tiga pengisi apabila pemuatan pengisi meningkat kepada 45wt% dengan nilai 5.25% (CaCO3), 2.94% (NS) dan 3.41% (Sibelite). Modulus tegangan komposit NS dan Sibelite menurun dengan peningkatan beban pengisi tetapi meningkat untuk komposit CaCO3.

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ABSTRACT

Usage of polymer material in food packaging field had been maintained from last decades until now. Biodegradable polymer had been investigated to replace original petrochemical polymer due to its affection to the environment. Polylactide Acid is one of the common biodegradable polymers that had been investigate for the usage of food packaging material. But PLA contains weakness on mechanical properties that affect the application of it. The aim of this research works is to investigate the effect of different loading of Polyethylene Glycol (PEG) and mineral fillers (Calcium Carbonate, Nepheline Syenite and Sibelite) on the mechanical properties of PLA. Fabrication of the composite is done by drying the materials in 50°C and melt-mixed with twin screw extruder. The materials produced were shape forming by using injection molding and hot press to form shape for tensile testing and impact testing. The particle of mineral fillers was characterized by Particle Size Analyzer (PSA) and Scanning Electron Microscope (SEM). The result showed that the addition of Calcium Carbonate causing increasing in tensile properties from 15wt% to 45wt% reached maximum at 36.47 MPa while addition of the other two fillers causing decreasing with increasing in fillers loading which reach 18.08 MPa (Nepheline Syenite) and 17.71 MPa (Sibelite). The elongation at break decreased for all three fillers when the filler loading increase to 45wt% with value 5.25% ($CaCO_3$), 2.94% (NS) and 3.41% (Sibelite). The tensile modulus of NS and Sibelite composite decreased with the increase of filler loading but increased for $CaCO_3$ composite.

CHAPTER 1

INTRODUCTION

1.1 Background

Food packaging responsible to keep food supply safety in the world. Food packaging protect food products from outside environment that are harmful and causes damage, in order to provide food with ingredients and nutritional information to all consumers (Coles, 2003). Food packaging also give consumers positive experience if it utilizes in good design and graphics. Therefore, materials used in food packaging become an important issue in technologies nowadays. The packaging materials must fulfil the requirement in field of mechanical, physical, and thermal resistance properties.

The traditional materials applied in food packaging technologies including glass, metal, paper, paperboards, and plastics (Kenneth, 2007). Among all the materials, plastics, or polymer had been chosen for food packaging due to advantage such as fluid and moldable, cheaper, and lightweight and consists wide range of physical and optical properties. Due to its advantages over other conventional materials, the usage of polymers as food packaging materials has significantly increased during the past few decades (Silvestre et al, 2011). Petroleum plastics become one of the most often utilised materials in the food sector for packaging (synthetic polymers). These types of polymers include polyethylene terephthalate (PET), low- and high-density polyethylene (LDPE and HDPE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS) (Housewirth, 2017). Due to their economical abundance, attractive presentation, excellent barrier characteristics against oxygen and aroma chemicals, softness, tensile and tear strength, lightness, and transparency, petrochemical polymers have been used in packaging materials for a long time (Tajeddin et al, 2020).

But the use of petrochemical polymers has many disadvantages such as poor water vapor transmission rate and contain negative effect on the environment. Non-biodegradable and non-composability are the worst properties to all these polymers. The problem faced by petrochemical polymers in food packaging had cause interest of engineers in the sustainable development of biodegradable polymers to replace the non-biodegradable polymers.

The term "biodegradable" indicated that the materials would break down by the enzymatic action of living organisms like bacteria, yeast, and fungi. Water (H_2O), carbon dioxide (CO_2), and biomass under hydrocarbon and aerobic circumstances or biomass and methane (CH_4) under anaerobic conditions are the end products of the breakdown process (Malathi et al, 2014). Biodegradable polymers were firstly introduced in 1980s. There are many sources of biodegradable polymer, from synthetic to natural polymers. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from nonrenewable petroleum sources.

Synthetic polymers consist of aliphatic polyesters that contain hydrolysable ester bonds that make them biodegradable. There are two class in aliphatic polyesters due to the bonding of the constituent monomers. The first class consist of polyhydroxyalkanoates which synthesized from hydroxyacids, HO-R-COOH. Example of them is poly (glycolic acid) (PGA) or poly (lactic acid) (PLA). Meanwhile, the second class consist of Poly (alkene dicarboxylate) which synthesized from polycondensation of diols and dicarboxylic acid. Example of second class synthetic polymer are poly (butylene succinate) and poly (ethylene succinate) (Vroman et al, 2009).

Poly (lactic acid) or polylactide (PLA) had been chosen as the fabrication materials due to its biodegradable properties. PLA is a hydrophobic polymer which usually obtained from polycondensation of D- or L-lactic acid or from ring opening polymerization of lactide, a cyclic dimer of lactic acid. Commercial PLA's glass transition temperature is about 63.8°C, elongation at break 30.7% and tensile strength is 32.22MPa (Briassoulis, 2004). PLA is a bio-based polymer made from starch or sugar that is non-toxic, compostable, and has a high level of mechanical strength and plasticity. It is accepted as GRAS (Generally Recognized as Safe) by the Food and Drug Administration (FDA) which suitable in food packaging. Besides that, PLA has excellent properties compared to other biopolymer such as environmentally friendly as PLA is biodegradable, recyclable and compostable; Biocompatibility as PLA did not cause any toxic or carcinogenic effect in local tissues; processibility as PLA has better thermal processibility and energy saving as PLA only requires 25-55% less energy to produce (Vroman, 2009).

The importance of mineral fillers in thermoplastic polymers had been investigated to promote the growth of applications. Addition of mineral fillers will affect most of the properties of the matrix phase beneficially or detrimentally. Usage of mineral fillers in polymer composite able to reduce overall materials cost as reduce usage in polymer materials, also able to improve the stiffness and flammability of final polymer product. Improvement in density, thermal expansion, optical changes, flame retardancy and mechanical properties also the example that can be changed through addition of mineral fillers into polymer (Civancik et al, 2018).

1.2 Problem Statement

Polylactide acid (PLA) had been developed convenient for many foods packaging company such as Danish dairy for yoghurt cups and other commercial food packaging and container (Jessen, 2007). However, compare to other polymer, bio-based and biodegradable polymer like PLA is more expensive than other fossil-based polymer on a weight basis. This is because of the complicated in the production process of PLA which include the ring opening polymerization process. Based on the price of biodegradable polymer in 2016, the price of PLA is about 2 EUR/kg with density about 1250 kg/m^3, meanwhile the price of polyethylene terephthalate (PET) is about 850 – 1050 EUR/ton with density about 1370 – 1390kg/m^3 (Vraag en aanbod, 2016). This shows that PLA are much lighter than other materials but with higher prices with will cost a lot in production of industry.

Therefore, the polymer composite system was implemented by adding mineral fillers. The addition of mineral fillers able to substitute most of the bio-based polymer used during the manufacturing process. The cost will be reduced as the polymer is less used after the addition of mineral fillers inside the composite system. Comparing mineral-filled polymers to unfilled polymers, the overall cost price is significantly cheaper. Mineral fillers able to reduce the usage of polymer which lead to reduction in cost, it also able to improve the mechanical properties of system by distributing mineral fillers into polymer matrix phase to create particulate polymer composite. Research also shown that the inclusion of mineral fillers into biodegradable polymers does not negate the microbial disintegration of polymers, which means that nature of filler will not affect the biodegradations rate of matrix polymer (Kuijpers, 2021).

Because PLA is a glassy polymer with weak elongation at break, many fields find it very hard to use. Therefore, toughening modification of PLA had been done investigation in recent years. One of the modifications is plasticization by addition of plasticizer. Addition of plasticizer is effective as it able to overcome the brittle nature of PLA and improve its flexibility. An excellent plasticizer is biodegradable, nonvolatile, nontoxic, and miscible with the polymer matrix.

1.3 Objectives

This research has been motivated by the fabricating biodegradable and high mechanical properties polylactide acid/minerals fillers composites by adding of Polyethylene Glycol (PEG) as plasticizer. The research performed is based on the idea outlined by the following objectives.

[1] To evaluate the effect of plasticizer (PEG) loadings on the properties of the PLA and determine the optimum PEG loading for fabrication of the composites.

[2] To investigate the effect of incorporating different type of mineral filler (Calcium Carbonate, Nepheline Syenite and Sibelite) into PLA/PEG composites.

[3] To evaluate the effect of mineral fillers loading on the properties of PLA/PEG composites.

1.4 Scope of study

In this research, addition of PEG in the PLA for plasticization and mineral fillers to improve mechanical properties by using twin screw extruder. The effect of plasticizer and mineral fillers on the improvement of PLA composite had been studied.

The materials of composite produced will be pelletized and undergoes injection molding and compression molding for further analysis. The particle size distribution and morphology of mineral fillers were characterized by using Malvern Particle Size Analyzer and High-resolution Scanning Electron Microscope (SEM). Next, tensile testing and impact test will be done on the sample for further analysis performance of composite on tensile strength and impact strength.

1.5 Thesis Outline

This thesis consists of 5 chapters. Chapter 1 introduces the general background of the study with concise introduction regarding the development of the research of biodegradable polymer in food packaging. Problem Statement as well as the objectives are also stated in this chapter. Chapter 2 presents the literature review on the general overview of biodegradable and non-biodegradable on food packaging which showing the properties of materials used in food packaging. Fabrication method available to mix well PLA together with PEG and mineral fillers. The types of plasticizers available in order to improve properties of pure PLA. Types of filler which mix with the biodegradable polymer to form composite. The shaping method of polymer composite. Chapter 3 consist of details regarding the materials utilized in this research as well as the experimental methods commenced during present the research. The experimental is discuss in this chapter are divided into several sections based on the objective of the research. Details on the sample fabrication procedure are explained methodically and illustrated in simple diagram. Chapter 4 discuss about the findings of present studies obtained during characterization process. The discussions are further divided according to the research objectives. The discussion covers several aspects include particle size analyse of mineral fillers, tensile properties, density and thermomechanical properties of the composites. Finally, Chapter 5 summarizes the highlights of this research as well as recommendation for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Polymer material in food packaging

Food packaging had been playing important roles in keeping food supply safely in the world for a longer period. This is because the main principal roles of food packaging are to protect the food products from outside contamination or damage and provide foods with ingredients and nutritional information to all consumers (Coles, 2003). Food packaging acts as protection from 3 major classes of external influences which are: chemical like gases (oxygen), light (visible, infrared or ultraviolet) and moisture (gain or loss); biological like microorganisms (pathogens and spoiling agents; physical from mechanical damage including shock and vibration encountered during distribution (Kenneth et al, 2007). Besides that, because food packaging serves as a channel of communication between the perception of a product and the company's history, it may have an impact on a customer's choice. (Eltayeb, et, al., 2009). This all shows that right selection of packaging materials will be able to maintains product quality and attract consumer’s attention.

From the traditional materials that have been used in food packaging, it includes glasses, metals such as aluminum, paper, and paperboards. Glass has extremely long history in food packaging as first glass made food holding are believed appeared around 3000 BC (Sacharow, et, al., 1980). Glass made container are produced by heating the mixture of silica, sodium carbonate and limestones in high temperature. Glass contain advantage such as chemically inert, able to withstand high temperature, rigid, able to produce in different shape and recyclable which are the advantages for food packaging application. But it is heavy and too brittles such easily breakage from pressure or impact. For metal materials, they are impermeable to moisture or gases, and it able to withstand high heat processing, but it only has limited shape compared to glass. For paper and paperboards, the materials have very good strength to weight characteristics, but it is too sensitive to moisture and loses strength when humidity increases which make it tears easily (Kenneth et al, 2007).

The packaging industry requires materials that has peculiar advantages over traditional materials, which is polymers (Silvestre et al, 2011). This is due to the distinctive qualities of polymeric materials, which include their low weight, excellent mechanical and thermal properties, resistance to corrosion, ease of handling, ease of manufacture, and affordability (Narayanan et al, 2017; Niranjana et al, 2016; Pilla et al, 2011). Manufacturing technology transformed the idea of packaging completely with the industrial revolution in the eighteenth century, and the development of polymer materials for packaging purposes started in the 1860s (Robertson, GL, 2003). For a long time, some of the petrochemical polymer, which also known as non-biodegradable polymer have served go-to packaging materials due to their economical abundance, desirable presentation, excellent barrier properties toward oxygen, aroma compound, softness, tensile and tear strength, lightness, and transparency (Jaben et al, 2015).

To reduce the environmental impacts caused by polymer-based food packaging, research had been done to employ biodegradable polymers as alternative materials to conventional fossil fuel-based plastics (Attran et, al., 2015; Siracusa et, al., 2008; Souza, et, al., 2016). Besides that, polymer composites, which combine pure polymers with nanomaterials and organic or inorganic chemicals, have also been investigated as fillers to improve the mechanical, thermal, and barrier properties of polymers. This shows the development of polymer in food packaging from non-biodegradable polymer to biodegradable polymer that indicates the requirement of environment in future.

2.1.1 Non-Biodegradable Polymer

Conventional synthetic undegradable polymer, also known as petrochemical polymer, are the types of polymers that belong to non-biodegradable polymer. They get their name from the fact that they are made of coal, natural gas, and fossil fuels. For a long time, petrochemical polymers have served as the main materials for food packaging due to their excellent characteristics in economical abundance, desirable presentation, barrier properties toward oxygen, aroma compounds, softness, tensile and tear strength, lightness, and transparency (Jabeen et al, 2015). The most common petrochemical polymers used for are low- and high-density polyethylene (LDPE or HDPE), polypropylene (PP), polyvinyl chloride (PVC), and lastly polyethylene terephthalate (PET) (Housewirth, 2017).

The petrochemical polymers mention above contains their own properties which provide different application in food packaging process. Table 2.1 shows the application of petrochemical polymer in food packaging field.

Table 2.1. Food packaging application of petrochemical polymers (Kumar et al. 2016)

Petrochemical Polymer	Packaging Application
Polyethylene Terephthalate (PET)	Soft Drinks bottles, Food jars, Microwaveable container
Polypropylene (PP)	Drinking bottles, Bottles for milk, Food container
Polyvinyl chloride (PVC)	Frozen food stretch films, Container lid
Low density polyethylene (LDPE)	Plates, Spoon, Bread bags
High density polyethylene (HDPE)	Grocery bag, Juice containers, Cereal and snack liners

Most of the synthetic polymer were designed to be lightweight, with good mechanical properties, high thermal stability and durability, and high resistance to environmental degradation (Raddadi, et. al., 2019). Strong covalent chemical bonds are used to join hundreds or thousands of organic monomers to form synthetic polymers. In fact, the compact and long carbon chains of synthetic polymer are difficult to degrade by microorganisms (Koushal et al, 2014). Most of the synthetic polymer that are disposed in nature has very unreasonably slow degradation process that requires long periods almost hundreds to thousands of years (Ncube et al, 2021). The polymer waste from food packaging mostly traditionally thrown away in landfill that required extensive periods of time following the composition of the plastic and the environment types and condition of disposal (Teija et al, 2008).

Instead of disposal method, there are other method to manage the waste of polymeric such like biological recycling, mechanical recycling, and thermos-chemical recycling (Achyut et al, 2010). But the recycling of polymeric product is not cost efficient, requiring high energy for transportation, sorting clean, and practically less performance level is achieved than the original product. The Life-cycle analysis (LCA) shows that the energy embodied of recycled plastics are about half than the energy of virgin materials due to the degradation of quality of the recycled materials (Dwivedi et al, 2019). Therefore, the production and consumption of recycled polymer materials is small, which same as show in Figure 2.1.

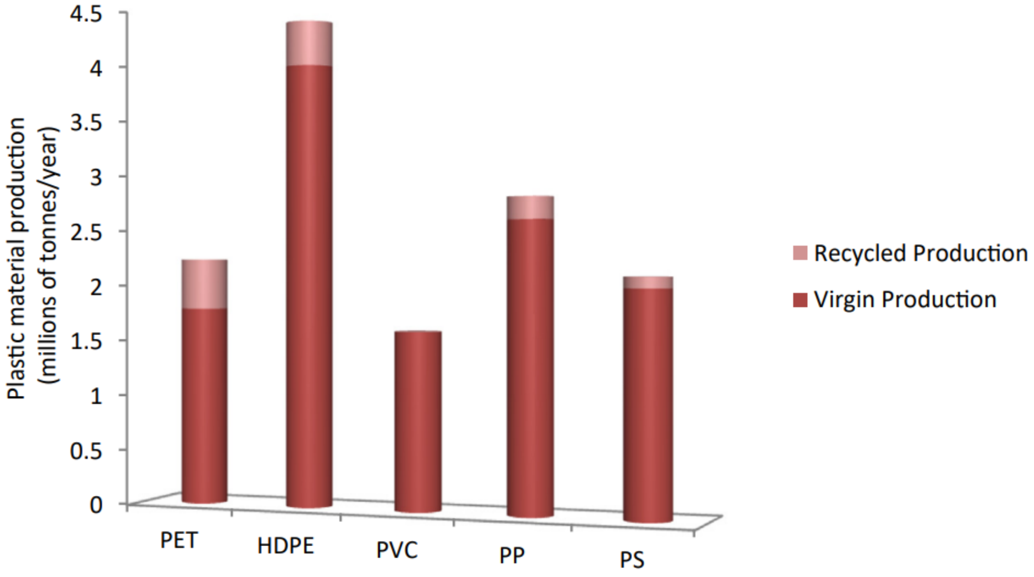


Figure 2.1: Contribution of recycling petrochemical polymers to consumption (Poushpi, 2019).

2.1.2 Biodegradable Polymer

Due to negative effect of non-biodegradable polymer to environment, biodegradable polymer was first introduced in 1980s. Typically, biodegradable polymers are produced using replenishable agricultural feedstocks, animals, waste from the marine food processing sector, or microorganisms. Biodegradable polymers are produced from renewable sources, with the properties almost same as conventional polymers (Kirwan, 2003). However, the cost of producing biodegradable polymers is more than twice as high as that of ordinary polymers, which also greatly reduces their marketability. (Zhang, 2020).

Biodegradable properties of polymeric materials is defined as its ability to be decomposed due to the action of microorganisms (Muhonja et al, 2018). During the biodegradation process, polymers are broken down into smaller molecular fragments (oligomers, dimers, and monomers) in the presence of specific enzymes secreted by microorganism, which are ultimately converted into bio decomposed products, such as water and carbon dioxide in aerobic conditions and biomass, methane, and hydrocarbons in anaerobic conditions (Ragaert et al, 2017; Muhonja et al, 2018). Figure 2.2 shows the mechanism of plastic biodegradation process due to attachment of enzymes to the surface and cleavage the polymer chains through assimilation of microorganism.

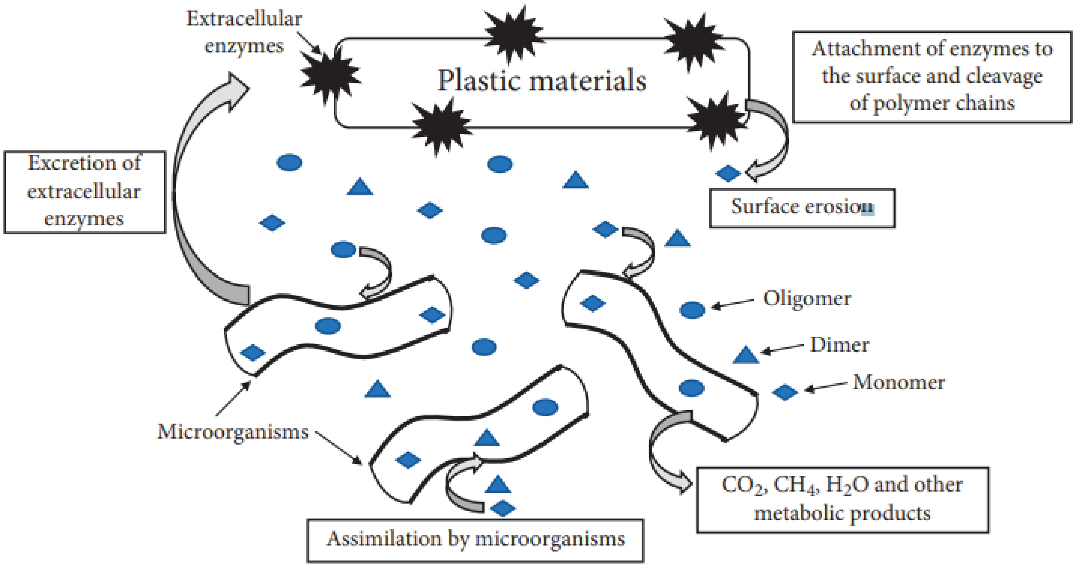


Figure 2.2: Mechanism of plastic biodegradation process (Alim et al, 2022)

Biodegradable polymers can be categorized based on their sources such like chemically synthesized polymers, extracted from biomass polymer and biosynthesized polymers. Table 2.2 shows the examples of biodegradable polymers from each category.

Table 2.2. Examples of biodegradable polymers for each class (Zhang et al, 2022)

Classified of biodegradable polymer	Example
Chemically synthesized	Polylactic acid (PLA), Polycaprolactone (PCL), Poly (vinyl alcohol) (PVA), Poly (glycolic acid) (PGA), Polybutylene adipate-co-terephthalate (PBAT)
Extracted from biomass	Cellulose, Starch, Chitin, Chitson, Gelatin, Collagen, Alginate
Biosynthesized from microbial fermentation	Polyhydroxyalkanoates (PHA), Bacterial Cellulose (BC)

Among all types of biodegradable polymers, polylactic acid (PLA) had been widely used compared to other types of biodegradable polymers. The PLA production global capacities experiences rapid growth to about 800k tonnes/year from 2011 until 2020, whereas the food packaging become the main application for PLA (Murariu et al, 2016). PLA has good mechanical properties such as high tensile strength and Young's Modulus, good flexural strength, that are even higher than the conventional polymer (Hamad et al, 2015). For packaging application, it is stated that PLA film have mechanical properties comparable to PET (Auras et al, 2004). PLA has a high molecular weight, high transparency, and very low water and gas permeability which is suitable for packaging material (Messin et al, 2020).

Although PLA acquire good properties, but it also contains properties such as brittleness and low thermal stability considered as disadvantage that need to be improved in application of food packaging materials.

2.2 Fabrication method of polymer composite with mineral fillers

Polymer-matrix composites with containing inorganic fillers had been investigated as their improving in characteristics, such as mechanical properties, thermal properties and chemical reagent resistance (Nielsen et al, 1994). The properties of polymer composite strongly depend on how the filler is presented in the polymer. The method used to combine filler and polymer will determine the microstructure developed, principally through exposure to the shear and elongational flow fields encountered during melt compounding (Hornsby, 2013). Melt mixing are one of the methods to fully produce the polymer composite.

There are different mixing scenarios happen during polymer compounding operation, which can be classify as extensive and intensive (dispersive). High molecular mass polymer in their molten state tends to be very viscous, and extensive mixing is achieved principally by convection. This is to achieve compositional uniformity or randomness of the particulate filler phase. For effective dispersion to occur, the molten polymer must first adequately "wet out" the fillers by covering surfaces and penetrating within the agglomerates of fillers. Once the agglomerates are broken down, the distribution of the resulting fragments occurs through randomization within the polymer matrix (Hornsby, 2013).

Extruders are common devices in food processing industries, and the utilization of extrusion process is particularly widespread in product manufacturing with polymer as raw materials (Chokshi et al, 2004). Extrusion is broadly used to produce film, sheet, pipe and profiles, and for specialty operations such as compounding, mixing and pelletizing. This method is called extrusion compounding, a preferred method to combine fillers with polymer, since the process is continuous and machinery design that offers considerable flexibility in terms of screw and barrel configuration to meet requirements demand from differing material types.

Screw extrusion process is one of the popular methods in fabrication of thermoplastics composites due to its cost effectiveness. The polymer grains will mix with reinforcement particles and fed to hopper in form of pellets. The mixture is then pushed forward by the feeding screw into the heated barrel and forced into split mould. The screw rotates and reciprocates during filling and after the extrusion process, until the materials cooled down. It had been analysed about the effect of screw extruder parameters on the tensile strength of fabricated filaments in figure 2.3.

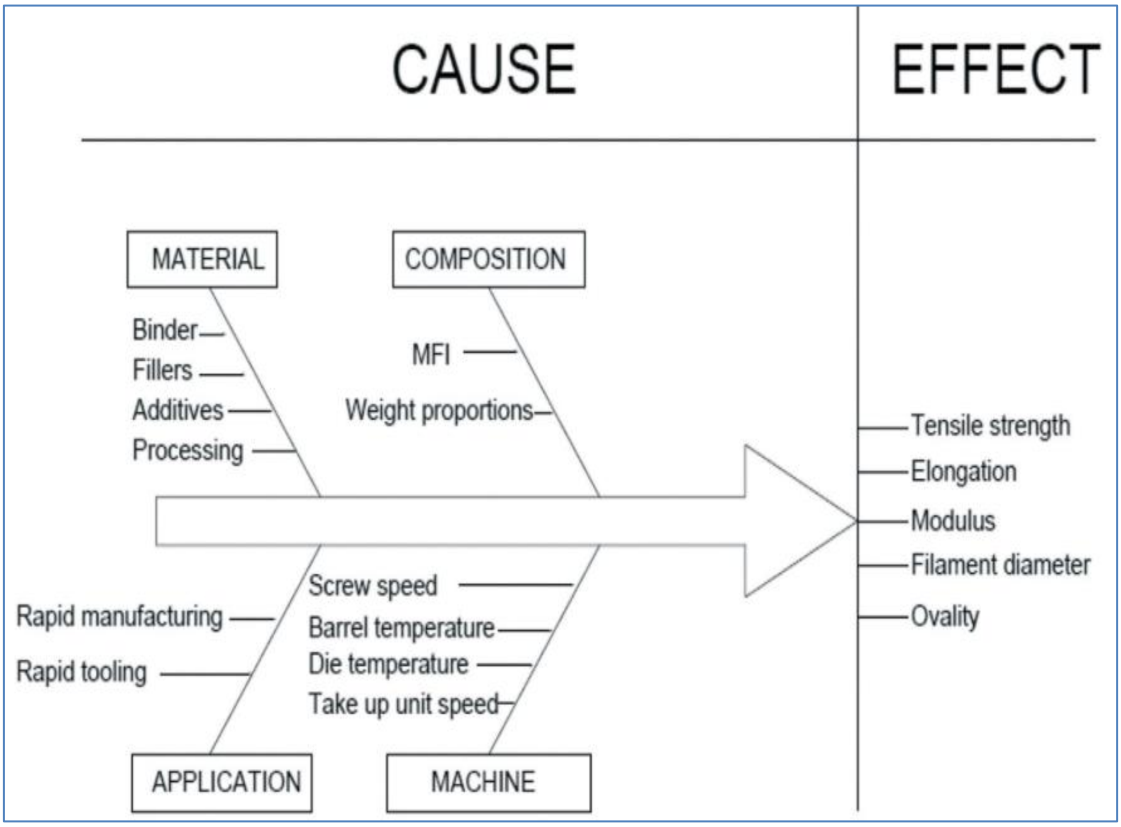


Figure 2.3: Cause and effect diagram of screw extrusion process for polymer matrix composite (Chohan et al, 2020)

2.2.1 Single Screw Extruder

The first analyses of extrusion process were related to classical flood-fed single screw extrusion and concentrated on the melt conveying process, and solid conveying (Wilczy, 2013). The earliest model for melting in single screw extruder was proposed by Maddock and Tadmor (Tadmor, 1966). Single screw extruder is the common type of extruder, and it offers relatively low investment cost.

Single screw extruders contain a single rotating screw in a metal barrel. Single screw extruder has a constant pitch and com in varying patterns. Figure 2.4 shows single screw extruder consist of three distinct sections, which are feeding or conveying stage, a plasticizing/transition stage, and a metering stage. Each section vary in channel depth (distance between the non-screw element and the wall of barrel). In feeding stage of extruder, the polymer in pellet or powder form is compacted together as the screw rotates, and the material is continuously introduced into barrel via the hopper. In transition section, the outermost portion of polymer melts and experiencing shearing. By following the time, the polymers will reach the metering section in the molten forms, and further shearing allows for greater stabilization of the polymer before it is ultimately extruded through a die and cooled (Lee, 2019).

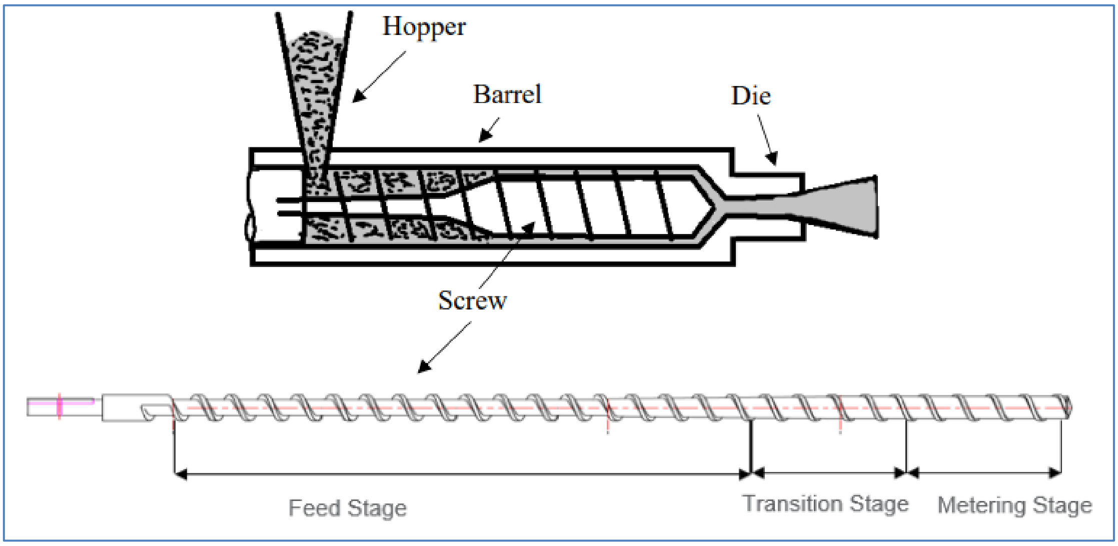


Figure 2.4: Schematic of a single-screw extruder with feed, transition and metering stage (Lee, 2019)

Standard single screw extruders have limited inherent mixing capability, developing only low level of shear strain and stress. They drag flow conveying action is also unsuitable for processing polymer with high fillers level. Conveyance of polymer through single screw extruders generally relies on a drag flow mechanism, involving frictional difference between the polymer and metal surfaces within the extruder. These exert a positive mechanical displacement action, being much less dependent on frictional characteristics of the material (Hornsby, 2013). The mixing action in single screw is poor and melting is slow, therefore twin-screw extrusion is needed.

2.2.2 Twin screw extruder

For more rigorous mixing where the shearing requirement is much higher than for single-screw extrusion, twin screw extruder is introduced. Twin screw extruders are commonly used in modern industry (Lewandowski, 2015). The mixing efficiency of a twin screw extruder can be increased by incorporating mixing elements along the screws. Twin screw extruders contain screw and barrel sections that are often modular which allow the machine design to be reconfigured to suit different filler polymer combinations. Twin screw extruder configuration consist of two screws which are orientated side by side in the extruder barrel with having a “figure-eight” cross section. The “figure-eight” cross section comes from the machining of two cylindrical bores who centres are less than two radii apart (Baird et al, 2003).

Twin screw extruders are classified by the degree to which the screws intermesh and direction of rotation of the screws. The screws can be corotating intermeshing, counterrotating intermeshing, or counterrotating non-intermeshing. All these provide greater mixing capabilities than single screw extruder and offer greater control over residence time distribution of the polymer (Lee, 2019). Figure 2.5 shows the three types of screw arrangements of twin screw extruder.

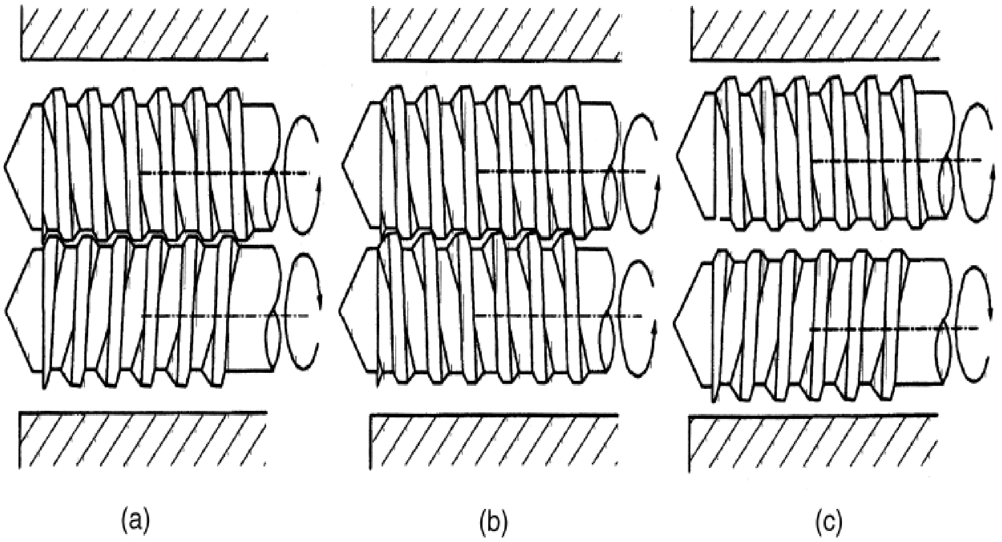


Figure 2.5: Various types of twin screw extruder: (a) counterrotating intermeshing. (b) corotating intermeshing and (c) counterrotating non-intermeshing (Baird et al, 1998)

The difference between twin screw extruder and single screw extruder is the type of transport that take places in the extruder. The drag-induced material transport of solid particles and molten material in single screw extruder consist of friction between the barrel wall and solid pellets in solid conveying zone, while viscous drag the molten state polymer. But in intermeshing twin screw extruder, the transport of material is considered to some degree positive displacement. The degree positive displacement is dependent on how well the flight of one screw closes the opposing channel of the other screw. The more closely the screws in extruders, the better the positive placement provided (Baird et al, 2003). Non intermeshing extruders resemble basically single screw extruders with not such so good transportability as the closely intermeshing screws.

Besides that, in twin screw extruder, the polymer velocity distribution is complex and difficult to describe mathematically. But complicated nature of polymer flow in twin screw extruder causes good mixing and devolatilizing abilities and are characterized by good heat exchange and fast polymer plasticizing (Lewandowski et al, 2022). Compared to single screw extruder, twin screw extruder has disadvantage such like expensive, structurally complex and difficult to manufacture.

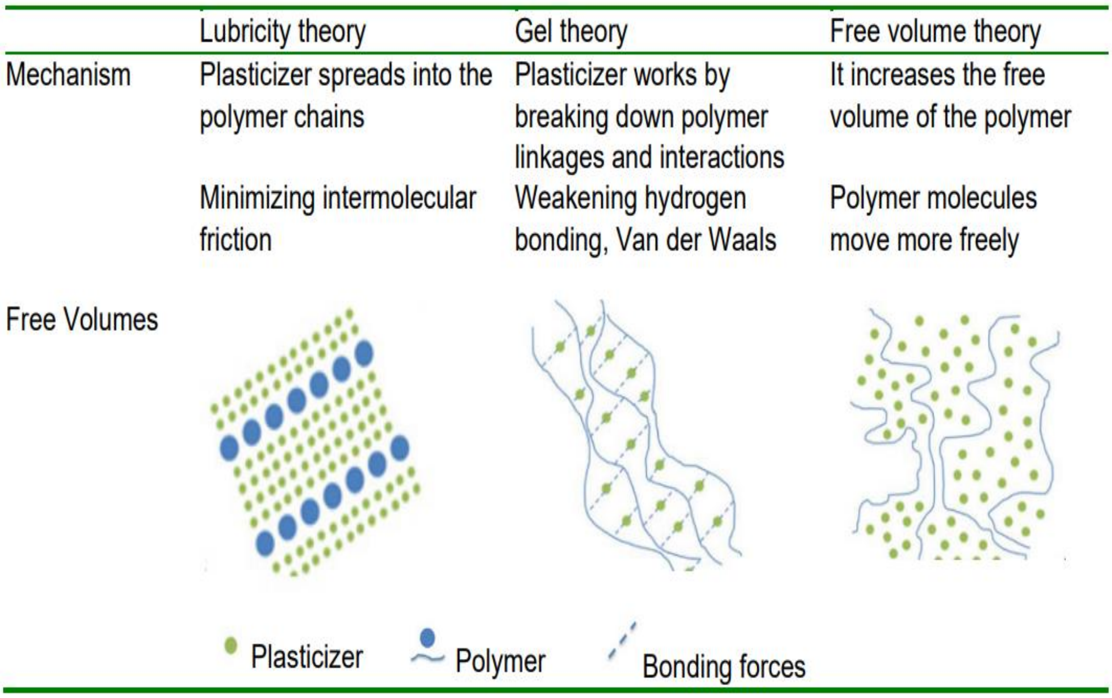
2.3 Plasticizer

Plasticizer is the substance which is incorporated into a material to improve properties of polymer such as flexibility, workability and distensibility (Rochow, 1976). The principal effect of addition of plasticizer is the change on the performance characteristics of plasticized product which make possible the use of polymers in applications where the previous three characteristics are required (Narvaez Rincon et al, 2015). The introduction of plasticizers into a polymer compound led to a change in the rheological properties of the bonds, improve the life span of the final product according to their application, and reduced energy consumption and material cost. The plasticizers able to reduce the brittleness and increased the heat resistance of its main materials. However, they reduced the thermal resistance and reduce dielectric properties (Bodaghi, 2019).

There are two main types of plasticizers, which is internal and external plasticizer (Bodaghi, 2019). Internal plasticizers attach to the polymer chains through a chemical bond and by polymer modification, increases the polymer’s elasticity. Meanwhile, external plasticizers are low vapor compounds that do not have any chemical reaction with the polymer and show their plasticizing properties only through physical interactions with the polymer (Sejidov et al, 2005).

Plasticizers are usually non-volatile high boiling point compounds, such as glycerol, glucose, amino acid, urea, etc. (Bangar et al, 2021). Many theories explained about mechanism of plasticizers and action on polymers such like lubricity theory, gel theory and free volume theory. The lubricity theory is assumed that the rigidity of the resin arises from intermolecular friction binding the chains of polymer together in a rigid network. During heating, the frictional forces are weakened to allow the plasticizer molecules to spread into the polymer chains. Once the plasticizer incorporated into the polymer, the plasticizer molecules shield the chains from each other, thus preventing the reformation of rigid network, which make it easier to move from one place to another (Sears et al, 1985). For gel theory, the plasticizers promote gel characteristics in polymer interaction, such as hydrogen bond and Van der Waals. The gel is formed by loose attachment occurring at intervals along the polymer chain. This facilitates the movement of plasticizer molecule, thus imparting flexibility (Harrison et al, 2002). For free volume theory, when a plasticizer is added, the polymer molecule of plasticizer moves freely, causing the free volume of the polymer to increase, making it more flexible and has ruby characteristics (Voirin, et al, 2016). All the mechanism of plasticizer shows in Figure 2.6 below.

Plasticizer had been applied to 60 polymers and more than 30 groups of products (Wypych, 2012). The plasticizer not only applied in petrochemical polymer, it also applied to most of the biodegradable polymer. All the petrochemical and biodegradable polymer with their plasticizer is shown in Table 2.3. It shows the versatility of phthalates, adipates, sebacates, azalates, glycol esters, and citrates able to plasticize petrochemical and biodegradable polymers. The plasticizer based on lipidic derivatives such as glycerol, vegetable oils, and lactic acid are selectively proceeded on biodegradable polymer.



	Lubricity theory	Gel theory	Free volume theory
Mechanism	Plasticizer spreads into the polymer chains Minimizing intermolecular friction	Plasticizer works by breaking down polymer linkages and interactions Weakening hydrogen bonding, Van der Waals	It increases the free volume of the polymer Polymer molecules move more freely
Free Volumes			

Figure 2.6: Plasticizer theory (Voirin, et al, 2016)

Table 2.3: Main polymer and their plasticizers (Voirin et al, 2016)

Plasticizer Types	PVC	PVB	PVA	PVDC	PVAc	PMMA	PLA	PHBV
Phthalates	/				/	/		
Adipates, sebacates, azalates	/	/		/		/	/	
Citrates	/			/	/		/	/
Glycol esters		/	/				/	/
Glycerol and its derivative							/	/
Lactic Acid							/	
Vegetable oils	/						/	/

Polylactic acid is nowadays the most famous environmentally friendly polymer that used for food packaging material in global. Its production and consumption drastically increased, and it is now a competitive material applied in convenience product. Packaging containers are commercially used below room temperature, therefore its mechanical performance under this condition is very important. For tensile modulus and flexural modulus, PLA has the highest value in comparison to PS, PP, and HDPE (Jamshidian, 2010). However, PLA based materials are rigid and brittle, plasticizer and fillers have been added to enhance the mechanical performance of PLA films. The usage of supporting materials such as plasticizer to improve poor properties of PLA has been researched to investigate the corporation of reinforcing materials to polymer. The plasticizers that commonly used by polylactic acid is polyethylene glycol (PEG), glycerol based toughening agent and ethylene-glucidyl methacylote copolymer (EGMA).

2.3.1 Polyethylene glycol (PEG)

PEG is one of the common plasticizers used for PLA which is biodegradable and nontoxic (Pillin et al, 2006). This fulfils the conditions for food packaging which able to maintain the food in safe condition before and after consuming the food product. PEG also have the advantages of a board range of molecular weight and miscibility (Jeung et al, 2014). The plasticization of PEG can effectively increase the chain mobility of PLA, and improve its ductility and drawability, thus broadening the range of potential application. There are some of the studies shows the properties improving by the PEG to the PLA and expand the application of PLA materials. It is well to know that PEG has very good miscibility with PLA because the terminal hydroxyl groups in PEG molecules can react with carboxyl groups in PLA molecules (Lai et al, 2004). The introduction of right amount of PEG can not only effectively improve the hydrophilicity, flexibility and impact toughness of PLA, but also enhance the degradation rate and crystallization kinetics of PLA (Jiao et al, 2015).

Jacobsen and Frtiz (1999) had used three different plasticizers which are poly (ethylene glycol) (PEG) (M_w 1.5 x 10^3), glucose monoesters and partial fatty acid esters to plasticize PLA through melting processing and investigate the influence of their types and loading (2.5%, 5% and 10%) on the mechanical properties of PLA. Through comparing PEG with the other two plasticizers, addition of 10% PEG to PLA brought the largest decreases in transition temperature, elasticity modulus and tensile strength, but greatest increases in the elongation at break (up to 180%) and impact resistance. This shows that the PLA become more ductile and not easy to break with the addition of PEG (Jacobsen et al, 1999).

PEG had a wide range of molecular weights (about 200 ~ 20000). Therefore, the molecular weight of plasticizer is an important factor that affects the crystalline and mechanical properties of polymer/plasticizer blend. Jiao et al. (2015) reported on the result of plasticization of polylactide acid (PLA) with PEG under different molecular weight (M_w 200 ~ 20,000 g/mol) and loading content (0wt% ~ 20wt%) by using twin screw extruder. The objective of the study is to investigate the effect of content and molecular weight of PEG on the crystallization and impact properties of PLA. The results revealed that PEG with molecular weight, M_w 10,000 could significantly improve the crystallization capacity and impact toughness of PLA. At 20wt% of PEG-10,000, the increases of V-notched Izod and Charpy impact strength are 206.10% and 137.25%.

Liang et al. (2015) also reported on the addition of PEG with different content (0, 5, 10, 15 and 20wt%) and molecular weight (M_w 6000, 10,000 and 20,000). PEG was mixed with PLA to form blend by twin screw extruder method. The effect of