SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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MECHANICAL AND MORPHOLOGICAL PROPERTIES OF POLYLACTIC ACID/ POLY(HYDROXYBUTYRATE-CO-HYDROXYHEXANOATE) BLENDS: EFFECT OF BLENDS RATIO AND MALEATED COMPATIBILIZER

By

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of the requirements for the degree of Bachelor of Engineering with Honours
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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Mechanical and Morphological Properties of Polylactic acid/ Poly(Hydroxybutyrate-co-Hydroxyhexanoate) blends: Effect of Blends Ratio and Maleated Compatibilizer**". I also declare that is has not been previously submitted for the award of any degree or diploma or other or other similar title of this for any other examining body or university.

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LIST OF SYMBOLS

Symbol	**Descriptions**
wt.%	Weight percentage
°C	Degree celsius
T_m	Melting temperature
rpm	Rotation per minute
T_g	Glass transition temperature
g/cm^3	density
MPa	Mega Pascal
GPa	Giga Pascal
g	gram
mm^2	Unit of area
mm/min	Crosshead speed
cm	Centimetre
mm	Milimetre
%	Percent

LIST OF ABBREVIATIONS

Abbreviation	**Descriptions**
PLA	Poly (lactic acid)
PHBHH	Poly (hydroxubutyrate-co-hydroxyhexanoate)
PLA-g-MA	Poly (lactic acid) grafted maleic anhydride
DCP	Dicumyl peroxide
MA	Maleic anhydride
PHA's	Polyhydroxyalkanoates
PET	Polyethylene terephthalate
PCL	Polycaprolactone
AcC	Acetyl cellulose
PHB	Poly (hydroxybutyrate)
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier transform infrared spectrum
SEM	Scanning Electron Microscope

SIFAT MEKANIKAL DAN MORFOLOGI ADUNAN POLILAKTIK ASID/ POLI (HIDROKSIKBUTIRAT-CO-HIDROKSIHEKSANOAT) : KESAN NISBAH CAMPURAN DAN PENSERASI

ABSTRAK

Kajian ini dijalankan untuk mengkaji nilai optimum adunan PLA /PHBHH pada sifat mekanikal, kesan nisbah campuran dan penserasi. PLA /PHBHH telah disediakan melalui kaedah pengacuan mampatan. Nisbah campuran 100/0, 75/25, 50/50, 25/75 dan 0/100 telah disediakan. Nisbah gabungan optimum PLA /PHBHH adalah kira-kira 75PLA/25PHBHH pada sifat tegangan 42.46 MPa. Kekuatan tegangan campuran berkurangan dengan penambahan nisbah gabungan PHBHH diikuti dengan modulus. Peningkatan komposisi PHBHH yang mempunyai kemuluran yang lebih tinggi meningkatkan kerapuhan PLA. Untuk ujian keliatan patah, nisbah gabungan 75/25 mempunyai nilai keliatan patah lebih tinggi pada 2.99 MPa.m$^{0.5}$. Penambahan penserasi PLA-g-MA dikaji untuk nisbah 75/25, 50/50 dan 25/75. Didapati bahawa penserasi meningkatkan tegangan dan keliatan patah sifat-sifat campuran polimer. Keputusan dapat dikuatkan lagi dengan pemerhatian morfologi. Daripada hasil FESEM, dapat dilihat bahawa penserasi yang meningkatkan lekatan fasa PLA dan PHBHH yang memberikan kesan ke atas sifat-sifat mekanikal campuran. Oleh itu, penserasi PLA-g-MA meningkatkan keserasian campuran PLA/PHBHH.

MECHANICAL AND MORPHOLOGICAL PROPERTIES OF POLYLACTIC ACID/ POLY(HYDROXYBUTYRATE-CO-HYDROXYHEXANOATE) BLENDS: EFFECT OF BLENDS RATIO AND MALEATED COMPATIBILIZER

ABSTRACT

This research was conducted to investigate the optimum of PLA/PHBHH blends on mechanical properties, the effect of blends ratio and the effect of maleated compatibilizer. The PLA/PHBHH were prepared by internal mixer. The blend ratio of 100/0, 75/25, 50/50, 25/75 and 0/100 were prepared. The optimum blend ratio of PLA/PHBHH on tensile properties is about 75PLA/25PHBHH with 42.46 MPa. The tensile strength of the blends decreases with addition of PHBHH blend ratio so as the modulus. The increment of PHBHH composition that having higher ductility improve the brittleness of PLA. For the fracture toughness testing, 75/25 blend ratio having higher fracture toughness value at 2.99 MPa.m$^{0.5}$. The addition of PLA-g-MA compatibilizer were studied for 75/25, 50/50 and 25/75 blends ratio. It was found that compatibilizer improved the tensile and fracture toughness properties of the polymer blend. The results can be supported by morphological observation. From FESEM results obtained, it was seen that the compatibilizer improve the phase adhesion of PLA and PHBHH that gives impact on the mechanical properties of the blends. Therefore, PLA-g-MA compatibilizer enhanced the compatibility of PLA/PHBHH blends.

CHAPTER 1

INTRODUCTION

1.1 Background

Since the 21st century, science and technology have changed toward renewable raw materials along with resources and processes which are more environmentally friendly and sustainable (Bledzki A.K et.al., 1999). The US Department of Energy (DOE) sponsored the Technology Road Map where it has aimed for 10 % of basic chemical building blocks from plant-based renewable sources to be achieved by 2020 (Zhang, Mohanty and Misra, 2012). Cellulose, protein and starch are natural polymers from plants and they have been re-examined not only as sustainable resources but also, as interesting safer materials with a variety of uses.

Natural polymer research and development, as it is well-known, is an early science. Now, it draws much attention for preparation of materials with new functions by using potent modern tools. (Eubeler *et al.*, 2009) mentioned that renewable resource (RR) is a modern term for an old subject that arose when the price of crude oil was raised between 1973 and 1979. RRs are products from plants and animals used for manufacturing purposes, including food products which are not utilized for nutrition, as well as food-processing wastes and co-products.

In accordance with technological advances and increasing world population, plastic materials have found its own significances in all aspects of life and industries. Nevertheless, the growth of conservative plastics in the environment like polyethylene, polypropylene, polystyrene, poly (vinyl chloride) and poly (ethylene terephthalate) are non-biodegradable in a way that is harmful and has been a threat to the Earth. In order to overcome all these potential problems, several strategies have been attempted. One of the strategies is to produce plastics with high degree of degradability.

The bio-plastics can consist of biodegradable plastics; that is to say, plastics made from fossil materials or perhaps, bio-based plastics which are produced from biomass or renewable resources. Figure 1.1 below shows the interrelated relationship between biodegradable and bio-based plastics. Despite the fact that polycaprolactone (PCL) and poly (butylene succinate) (PBS) are petroleum-based, they can actually be degraded by microorganisms. Poly(hydroxybutyrate) (PHB), poly(lactide) (PLA) and starch blends, conversely, are produced from biomass or renewable resources and thus, they are biodegradable. Moreover, polyethylene (PE) and Nylon 11 (NY11) can also be produced from biomass or renewable resources, yet they are non-biodegradable. Acetyl cellulose (AcC) can be biodegradable or non-biodegradable whereby it depends on the degree of acetylation. AcCs with low acetylation can be degraded whereas non-biodegradable AcCs are those with high acetylation (Tokiwa *et al.*, 2009).

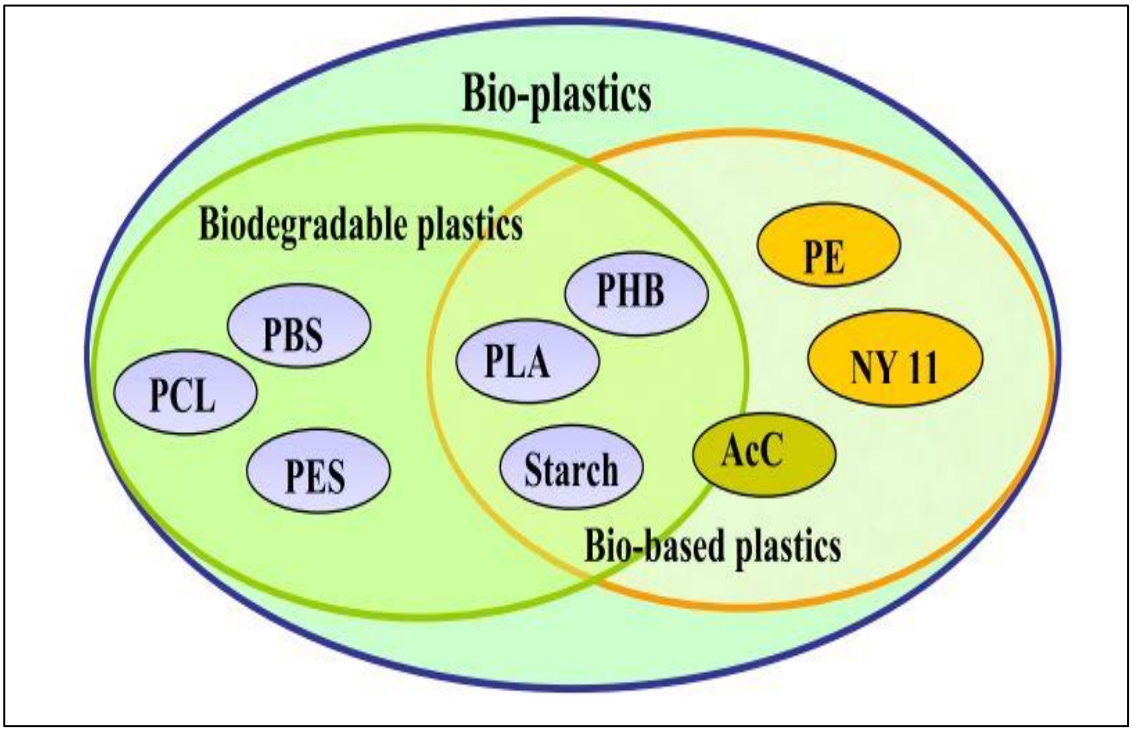


Figure 1.1: Bio-plastics can consist of biodegradable plastic and bio-based plastics (Tokiwa *et al.*, 2009)

Because biodegradable plastics are environmentally friendly, many people have seen them as a capable solution to the aforementioned problem. Biodegradable plastics can be obtained from renewable feedstocks; hence, they help to reduce greenhouse gas emissions. For example, agricultural products and microorganisms can produce polyhydroxyalkanoates (PHA) and lactic acid (raw materials for PLA) through fermentative biotechnological processes.

It cannot be denied that polymer/polymer blending method is effective in enhancing the original physical properties of one or both of the components, or producing new polymeric materials which have broadly diverse properties without being parallel in homopolymers (Dunford, 2012). Basically, there are two ways to make a blend, particularly by mixing the components in a softened or molten state and then, blending the components from their solutions.

Composites based on cellulose and other natural polymers which are environmentally friendly and can substitute for the polymers from petroleum have received a lot of attention. In spite of that, poor solubility in organic solvents and low thermal decomposition temperature lying below the melting point are the properties found in cellulose. Both properties make it difficult to disperse cellulose in melted polymers, requiring a suitable solvent system.

Both PLA and PHB are biodegradable polyesters and they are used in consumer products by some industrial sectors remarkably because of their biodegradability, biocompatibility and sustainability. They are comparable to certain conventional polymers in terms of thermal and mechanical properties. This has brought about a great deal of people’s interest to explore the physical and processing properties of PLA and PHB for other potential applications. Since PLA and PHB have poor properties such as, brittle in room temperature, number of modifications have been planned to make their processing and mechanical properties better. Among the modifications include the polymer blending and the addition of compatibilizer.

1.2 Problem Statement

Plastics are one of the utmost inventions in the 20th century. The existence of plastics enables the making of products which completes the needs of the public for plastic applications. Plastics make our life easier that we can buy food and drinks put in lightweight, clean and safe containers or wrapped in the packaging, all made of plastics. Even vehicles which are comfortable and pleasing to the eye that we can drive or ride around are created partly from plastics. Besides, small electronic devices that allow us to communicate and keep connected with people as well as entertain us in the real or “fantasy” world are also part of plastics.

Plastics are lightweight and thus, other heavier debris sometimes steals their role. Although plastics can be recycled and reused many times, being lightweight can cause plastics to be airborne and difficult for waste management companies to collect and dispose them of in landfills or other disposal environments. To explain further, the lightweight plastics can take up the most space in landfills, later resulting in a serious litter problem in lands and seas. Floating plastic debris might be the last legacy of our society. Through proper education and training, we can help our young generation become sustainable. We can educate them about the production of products and services with reduced environmental impacts like those with minimal waste dumping and greenhouse gas emission and also, anti-pollution products.

Nowadays, bio-plastics can be made from corn, soy, sugarcane, potato or other renewable material sources. If petroleum plastics, for instance, are made from renewable or recycled material sources, they along with the manufacturing process itself can also be sustainable. Plastics have the opportunity to be produced as sustainable materials when renewable or recycled materials sources and lower energy are used. Besides of having a low carbon footprint and producing less pollution, sustainable plastic materials can be recycled or composted at the end of its service life.

In this new era of science and technology, biodegradable blends have been developed through the combination of both biodegradable plastics. Polymer blends are capable of equipping materials with useful properties which are beyond the normal range that can be attained from single polymer equivalents. The composition together with different blending ratio and maleated compatibilizer used will affect the polymer blend properties which involve mechanical and other physical properties.

Poly (lactic acid) (PLA) is a biodegradable and biocompatible crystalline polymer that can be produced from renewable resources and has become a great interest to the industry owing to its availability and low cost. Among the environmental advantages of PLA include low energy usage for its production and reduced greenhouse gas emission apart from its opportunities for the future. PLA performs the function of packaging materials in agriculture, textile industry (fibres), medicine (scaffolds) and pharmacology (Gerard *et al.*, 2014). However, the weak points of PLA are found to be high brittleness, slow crystallization rate and high permeability to gases. The solutions to these problems are by using plasticizers, making composites, copolymerizing with other components and blending with other polymers.

A typical biodegradable thermoplastic polymer is poly(hydroxybutyrate-co-hydroxyhexanoate) (PHBHH) formed from microorganisms. It is produced by copolymerizing hydroxyhexanoate to poly(hydroxybutyrate) (PHB) (Wellen, Canedo and Rabello, 2015). The copolymerization is able to resolve the hard and brittle characteristics of PHB. Furthermore, the processing temperature of PHB can also be minimized. However, PHBHH remains to be brittle even after the copolymerization process. Hence, the idea of blending PLA with PHBHH is introduced, provided that PHBHH is less brittle than PLA, in order to improve the ductility and produce fully biodegradable polymer blends.

A number of blending ratios can be used for better miscibility of polymer blends. In this research, PLA is blended with PHBHH. The effects of the blends ratio itself and maleated compatibilizer used on polymer blends, followed by the morphological and mechanical properties of the polymer blends are studied in detail.

1.3 Research Objectives

The aim of this study is to investigate the optimum of PLA/PHBHH blends on mechanical properties, the effect of blends ratio and the effect of maleated compatibilizer. The objectives are clearly stated as below:

i. To study the optimum composition of PLA/PHBHH blend in term of its mechanical properties.
ii. To evaluate the effect of PLA/PHBHH blend ratio (75/25, 50/50, 25/75) from the aspect of tensile, fracture toughness and morphological properties.
iii. To examine the effect of maleated compatibilizer on tensile properties, fracture toughness and morphological properties of PLA/PHBHH blend.

1.4 Scope of Work

The combinations of PLA and PHBHH with different blend ratios were prepared to investigate its effect on mechanical testing and morphological observation. In this research, the PLA/PHBHH were prepared using an internal mixer. To improve the compatibility between the two polymers, the compatibility of the polymer blends was achieved by using an incorporating compatibilizer. Several mechanical tests were carried out to examine all the prepared blends which includes tensile and fracture toughness, accompanied by a morphological observation.

1.5 Thesis Structure

There are five chapter provided in this thesis and each chapter information related to the research interest which includes;

i. Chapter 1: A brief overview about research background, problem statement, research objectives, scope of work and thesis structure.
ii. Chapter 2: Literature review. It covers brief explanations regarding biodegradable polymer and experimental procedures in this study.
iii. Chapter 3: Methodology of research work and equipment used.
iv. Chapter 4: Experimental results and discussions.
v. Chapter 5: Conclusions of this research work and suggestion for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

(Rudnik, 2007) described thermoplastic polymers as soften and process under the action of heat and pressure. Upon cooling, the polymer hardens and takes the shape of the mould. When thermoplastics are compounded with appropriate ingredients, they can generally endure some of the heating and cooling cycles without experiencing any structural failure. Thermoplastic polymers are used largely in many applications because of its easiness to be processed into products and durability to go through repeated cycles of softening and hardening.

Thermoplastics usually degrade under high temperature condition easily. (Chanda and Roy, 2006) supported that by combining thermoplastics with appropriate ingredients, the materials can withstand several heating and cooling cycles without any structural failure during compounding. Moreover, thermoplastics can be used alone, used as matrix in polymer composite or mixed together to produce polymer blends.

The most common use of thermoplastics is petrol-derived polyolefin which consists of polypropylene, polyethylene and others. The use of thermoplastics depends on the types of application, service performance and cost. The main problem of polymers is pollution caused by its hardness to degrade in ambient temperature and thus, a new version of thermoplastics known as bio-based or biodegradable plastics has been spread commercially for its environmentally friendly properties (Avarez-Chavez *et al.*, 2012).

All polymers possess different tensile and thermal properties. Unfortunately, polymers cannot satisfy the desirable properties with only one type of polymer. In order to create polymers with such properties, two or more kinds of polymers are combined and this is called polymer blends.

2.2 Bio-based plastics

Plastic is a general name attributed to different polymers with high molecular weight which can be degraded through various processes. Nonetheless, taking the abundance of plastics in the environment and their specificity in attacking plastics into consideration, the most effective process turns out to be biodegradation of plastics by microorganisms and enzymes. When plastics are utilized as substrates for microorganisms, their biodegradability should be evaluated not only based on the chemical structure but also, the physical properties.

Innovation in plastics will definitely make a great contribution to the increasing economic growth and life quality as well as solve or at least, reduce the environmental issues. Now, there is a remarkable increasing demand for biodegradable polymers in many areas such as medicine, pharmacy, agro chemistry and packaging industry. These fast-growing scientific areas are related to today's crucial health and social issues (Rychter *et al.*, 2006).

When new environmentally friendly and sustainable plastics are introduced in the packaging and end-user industries, they have become a solution to major problems concerning waste management. Spreading information as well as identifying and removing the barriers appear to be helpful towards more widespread use of sustainable plastics which are based on particularly biodegradable or renewable resources. Ecological concerns have also resulted in people's interest in products from renewable resources. Looking from the perspective of sustainable development, biodegradable polymers are regarded safe for the environment and become a preferable alternative to conventional polymers (Musioł *et al.*, 2015).

Starch is one of the bio-based plastic Starch-based polymers can be produced from potato, corn, wheat, cassava, or tapioca. In the United States and Europe, corn starch is the predominate source for starch-based polymers. Corn starch is mostly used for animal feed. Starch-based polymers can be processed on traditional thermoplastic forming operations of injection molding, extrusion, blow molding, compression molding and rotational molding. Starch can be made from corn or vegetable oils and other renewable sources. The most common plasticizers for starch are water and glycerol (Rychter *et al.*, 2016).

Starch-based plastics can be classified as compostable if the additives are also biodegradable under industrial compost environment conditions. Starch can be an additive for petroleum-based plastics like polyethylene, polypropylene, polyurethane, and polyester. However, these starch-filled petroleum-based plastics are not biodegrade under industrial composting conditions and would not be recyclable with commercial mechanical recycling operations (Wu, 2009).

The use of bio-based and biodegradable polymers in food packaging is currently growing to lessen the consumption of non-renewable resources and avoid plastic waste from piling up. At the same time, the food packaging industries also require the development of simple packaging formulation, formed by easy, readily available and economical processing technologies like melt blending approaches (Arrieta *et al.*, 2014)

Because biodegradable plastics are environmentally friendly, many people have seen them as a capable solution to the aforementioned problem. Biodegradable plastics can be obtained from renewable feedstocks; hence, they help to reduce greenhouse gas emissions. For example, agricultural products and microorganisms can produce polyhydroxyalkanoates (PHA) and lactic acid (raw materials for PLA) through fermentative biotechnological processes. Biodegradable plastics offer many benefits which include increased soil fertility, low amassing of bulky plastic materials in the environment (while reducing possible injuries to wild animals) and cost cutting of waste management.

2.2.1 Poly (lactic acid) PLA

Polylactic acid (PLA) is a rigid thermoplastic polymer that can be semi-crystalline or completely amorphous where it relies on the stereo purity of the polymer backbone. L-lactic acid (2-hydroxy propionic acid) is the natural and most prevalent form of the acid. Meanwhile, D-lactic acid can be produced either by microorganisms or through racemization and this “impurity” performs similarly as co-monomers in other polymers namely, polyethylene terephthalate (PET) or polyethylene (PE). In PET, for the purpose of controlling the rate of crystallization, diethylene glycol or isophthalic acid is copolymerized into the backbone at low levels between 1 % and 10 %. Likewise, D-lactic acid units are combined into L-PLA considering the optimization of the crystallization kinetics for certain fabrication processes and applications.

PLA is a unique polymer that acts more likely as PET and simultaneously, it also performs nearly the same as polypropylene (PP); a polyolefin. PLA may be the polymer with the largest array of applications due to its capability to be stress-crystallized, thermally crystallized, impact modified, filled, copolymerized and processed in most polymer processing equipment. In addition, it can be formed into transparent films and fibres or perhaps, injection moulded into blow mouldable preforms for bottles like PET. PLA is also well-known for its organoleptic characteristics and applications in food contact or food-related packaging (Henton *et al.*, 2000).

On the other hand, the commercial feasibility has been restricted as a result of high production cost; that is greater than $2/lb. Until now, PLA has somehow replaced petroleum-based plastics in commodity applications and its initial use is also found in biomedical applications such as sutures (Cycles *et al.*, 2006).

Poly (lactic acid) (PLA) shows a balance of performance properties, equivalent to those of traditional thermoplastics. PLA can be fabricated in various familiar processes and generates a new combination of properties for packaging which include stiffness, clarity, dead fold and twist retention, low temperature heat sealability, aside from another combination of barrier properties like flavour, aroma and grease resistance. PLA polymers extend from amorphous glassy polymers with a glass transition temperature of about 50-60 °C to semi crystalline products with melting points of between 130 to 180 °C, determined by the sequence of enantiomeric repeating units (L and D) in the polymer backbone.

In point of fact, PLA has good mechanical properties, thermal plasticity and biocompatibility. It is readily fabricated and thus, has turned out to be a highly favourable polymer for a variety of end-use applications. In terms of the physical property, PLA is usually loose compared to polystyrene. A standard-grade PLA has high modulus and strength but like polystyrene, it lacks toughness. On the positive side, orientation, blending or copolymerization are believed to be capable of improving the toughness of PLA.

In this new “green chemistry” world which portrays concern for the environment, PLA has additional features making it unique in the marketplace. The starting material for the final polymer; lactic acid, is made by using 100 % annually renewable resources through a fermentation process. The polymer degrades rapidly in the environment and is eventually converted to carbon dioxide and water, given that the by-products are of very low toxicity.

Figure 2.1 presents how PLA can be prepared by direct condensation of lactic acid and by the ring-opening polymerization of the cyclic lactide dimer. It is difficult to remove the trace amounts of water in the late stages of polymerization and limits the ultimate molecular weight because the direct condensation route in the approach said earlier is an equilibrium reaction. Although other approaches like azeotropic distillation which aims to drive the removal of water in the direct esterification process have been evaluated, the ring-opening polymerization of lactide still becomes the focus of most work. To enumerate, Cargill Dow LLC has developed a patented, economical continuous process to produce lactic acid-based polymers. This process involves the integration of substantial environmental and economic benefits gained from synthesizing both lactide and PLA in the melt rather than in solution.

Accordingly, a commercially, sustainable biodegradable commodity polymer is made, for the first time, from renewable resources. Regarding the process, it begins with the fermentation of dextrose to produce lactic acid and it is followed by a continuous condensation reaction of aqueous lactic acid for the formation of PLA prepolymer with low molecular weight. By using a catalyst, the low molecular weight oligomers are converted into a mixture of lactide stereoisomers in order to boost the intramolecular cyclization reaction rate and selectivity. Then, vacuum distillation is taken place to purify the molten lactide mixture. By using an organic catalyzed and ring-opening lactide polymerization in the melt so that the use of costly and environmentally unfriendly solvents is eliminated completely, high PLA polymer is finally produced. After the polymerization is finished, the process proceeds with any remaining monomer being removed under vacuum and recycled to the early process.

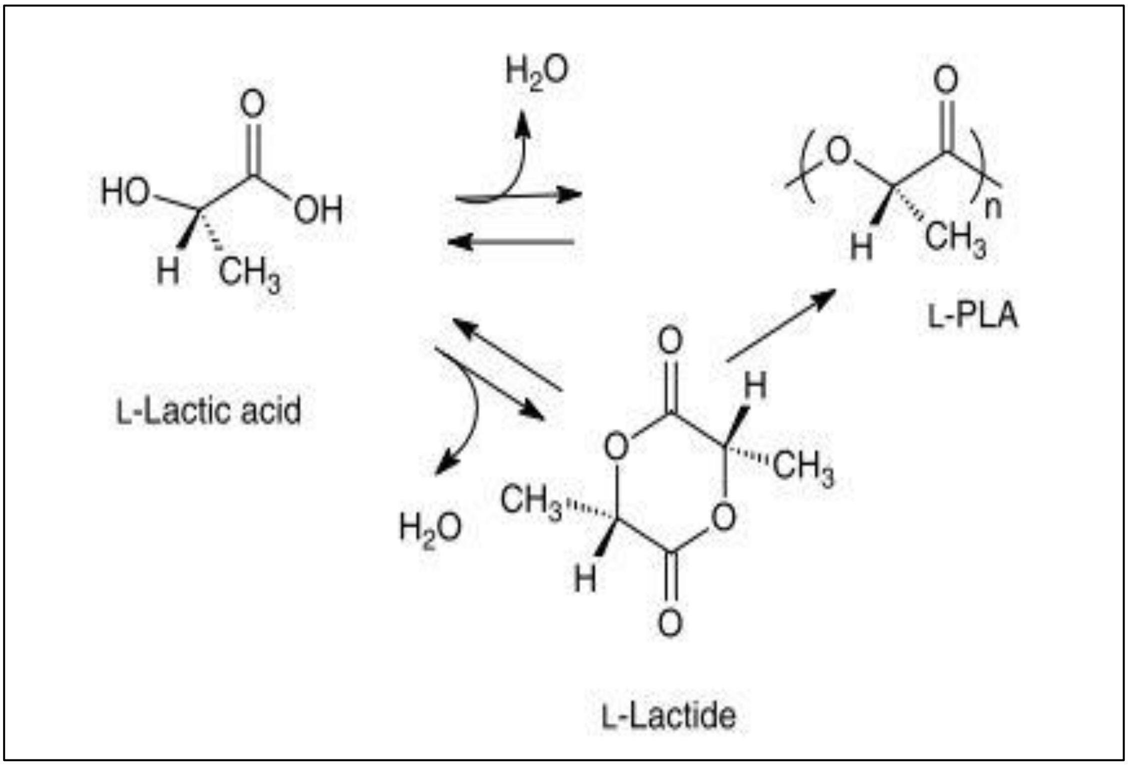


Figure 2.1: Polymerization routes to polylactic acid (Cycles *et al.*, 2006)

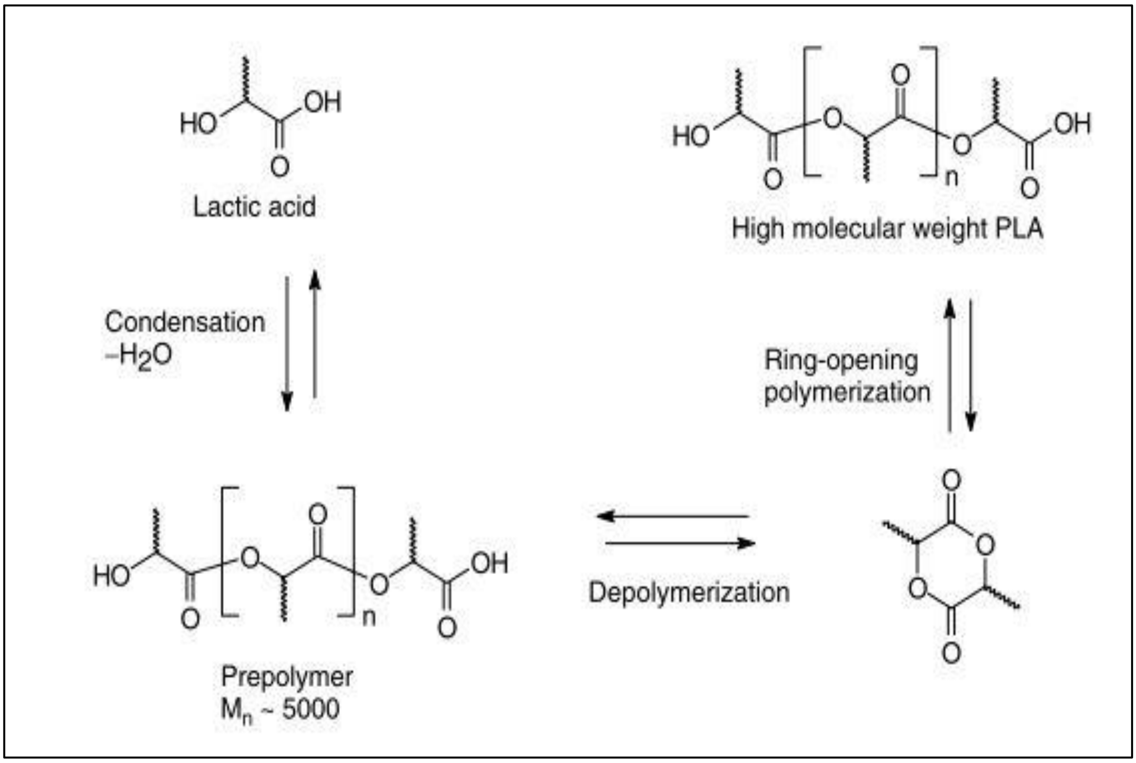


Figure 2.2: Schematic of PLA Production via prepolymer and lactide (Cycles *et al.*, 2006)

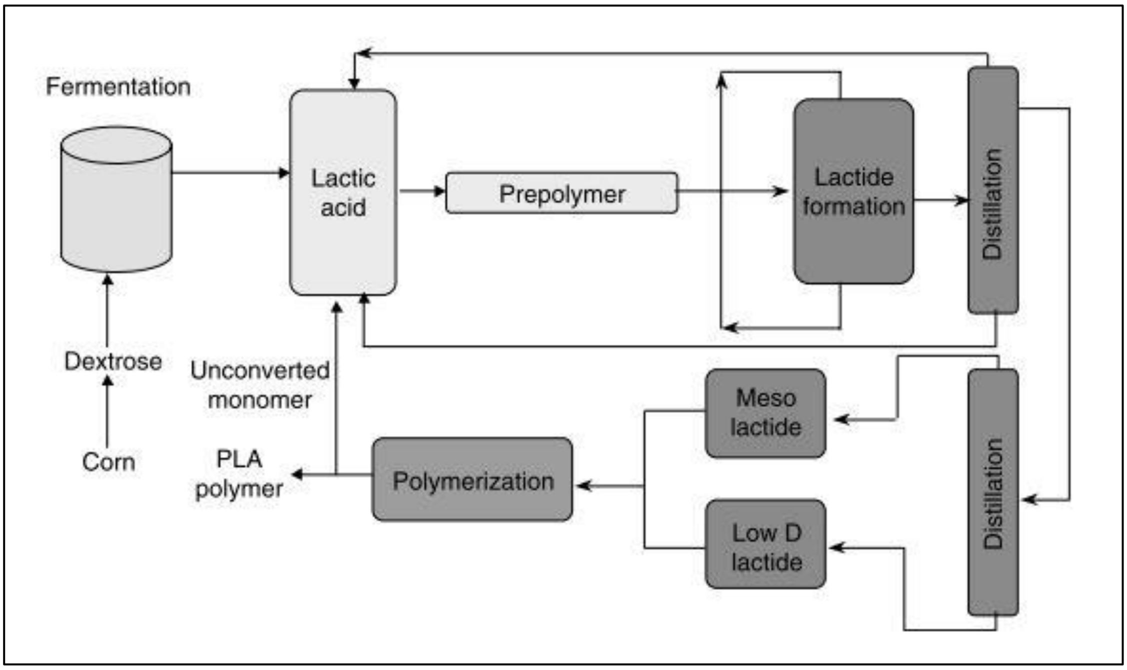


Figure 2.3: Non solvent process to prepare polylactic acid (Henton *et al.*, 2000)

Poly (lactic acid) products are looked forward to its uses in many applications such as packaging, paper coating, fibres, films and a host of moulded articles. The first products were intended for packaging films and fibres for textiles and non-woven. For packaging films, it makes clear films with good barrier yet low heat-seals properties whereas for fibres, it brings about apparels with better drape and moisture management as well as industrial clothing which impart better UV resistance, reduced flammability and good resistance to soiling and staining (Ren *et al.*, 2015).

PLA production comprises the fermentation of agricultural products like corn, potato, cane sugar and rice. Indeed, high bio-compatibility and biodegradability of PLA make it useful for both biomedical and packaging applications. Similarly, as polyolefins, PLA can also be readily processed.

Despite this list of advantages, high production cost, brittleness and low thermal stability of PLA limits its application. The addition of renewable and biodegradable fillers can improve the cost-performance balance instead of the mechanical and thermal behaviours. The examples of such fillers are cellulose or cellulose derivatives (Frone *et* *al.*, 2013). Natural fibres, taking over synthetic fibres like glass, have been used in polymer composites. Among the advantages, which have made natural fibres receive a lot of attention, are abundance, renewability, high stiffness, low density, low cost, non-abrasiveness to the processing equipment and possibility to be incinerated.

2.2.2 Poly (hydroxybutyrate-co-hydroxyhexanoate) (PHBHH)

The family of polyhydroxyalkanoates (PHA) holds various mechanical properties ranging from hard crystalline to elastic, which hinge on the composition of monomer units. Solid-state poly(3-hydroxybutyrate) (P(3HB)) is a compact right-handed helix with a two-fold screw axis (whereby two monomer units complete one turn of the helix) and a fibre repeat of 0.596 nm. Because of its stereo regularity, P(3HB) comes to be a highly crystalline material. Its melting point is close to that of polypropylene, precisely around 177 °C even though the biopolymer is stiffer and more brittle.

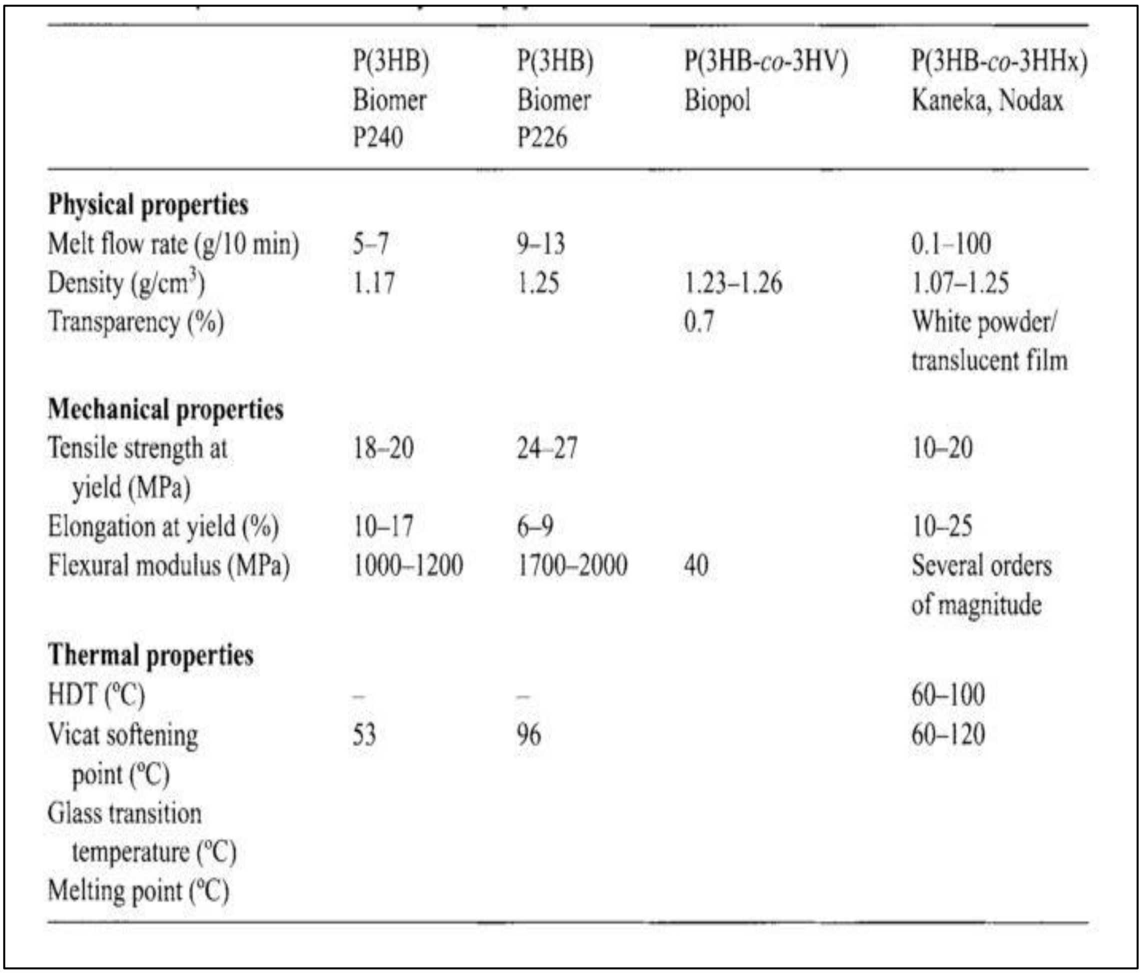
There are also other properties that P(3HB) and polypropylene share in common. The densities of crystalline and amorphous PHB are 1.26 and 1.18 g/cm^3 respectively. Furthermore, P(3HB) is water insoluble and rather resistant to hydrolytic degradation. Hence, this differentiates P(3HB) from most bio-based plastics which are currently available as either moisture or water soluble.

Mechanical properties of PHB like young’s modulus and tensile strength are almost the same as that of polypropylene even if its extension to break is significantly lower than that of polypropylene. However, PHB is a stiff and brittle highly-crystalline polymer by reason of the high stereo regularity of its biologically produced macromolecules. PHB is also thermally unstable during processing. Moreover, the molecular weight of PHB degrades markedly at temperature just above the T_m. This poor property limits one of its main applications as biodegradable polymers; that is the use of PHB in flexible films.

Consequently, a lot of efforts to upgrade its mechanical properties have been made, especially by copolymerizing a comonomer with PHB monomer. One of the ideas is using a bulkier comonomer to reduce the crystallinity and possibly increase the flexibility of the resulting copolymers.

The first attempt was the copolymerization with 3-hydroxyvalerate (3-HV) performed by ICI in the early 1980s. Due to the isodimorphism of the P (HB-co- HV) copolymer, the crystallinity of poly (3-hydroxybu- tyrate-co-3-hydroxyvalerate) (P(HB-co-HV)) does not once fall below 50 %. It is revealed that poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHB-co-HH) shows a greater T_m at a given mol % comonomer, when compared to P(HB-co-HV). Besides, it is interesting to point out that hexanoate and larger comonomers, regardless of their molecular sizes, depress T_m in the same manner. This feature proves the breakdown of the isodimorphism which occurs in the P(HB-co-HV) copolymer, involving the combination of comonomer units with three or more carbon units.

Table 2.1: The properties of commercially PHAs (Rudnik,2008)



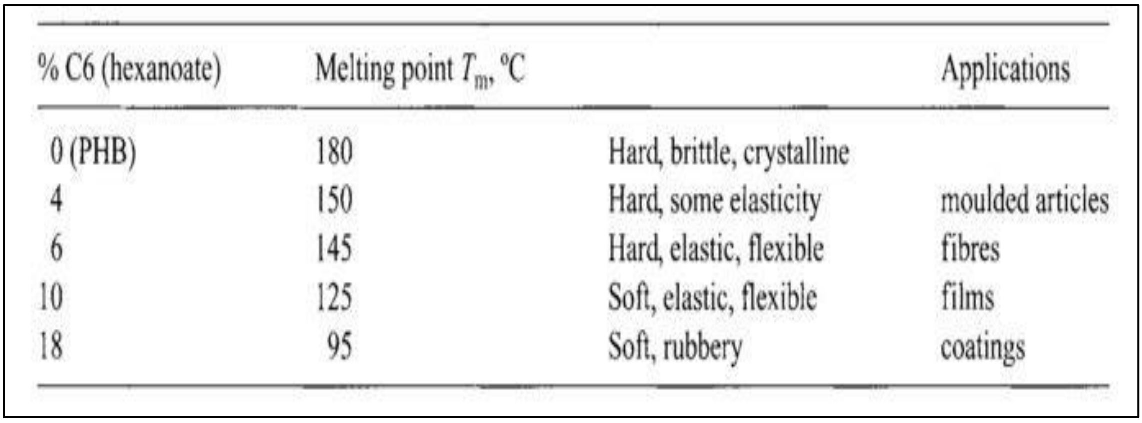
	P(3HB) Biomer P240	P(3HB) Biomer P226	P(3HB-*co*-3HV) Biopol	P(3HB-*co*-3HHx) Kaneka, Nodax
Physical properties				
Melt flow rate (g/10 min)	5–7	9–13		0.1–100
Density (g/cm^3)	1.17	1.25	1.23–1.26	1.07–1.25
Transparency (%)			0.7	White powder/ translucent film
Mechanical properties				
Tensile strength at yield (MPa)	18–20	24–27		10–20
Elongation at yield (%)	10–17	6–9		10–25
Flexural modulus (MPa)	1000–1200	1700–2000	40	Several orders of magnitude
Thermal properties				
HDT (°C)	–	–		60–100
Vicat softening point (°C)	53	96		60–120
Glass transition temperature (°C)				
Melting point (°C)				

Improvement in properties such as crystallinity, melting point, stiffness and toughness can be achieved through the formation of PHA copolymers by incorporating other hydroxy-acid units. As the fraction of 3HV increases, the impact strength of copolymer also increases and there is a decrease in Young's modulus. In other words, copolymer becomes tougher and more flexible.

The rise in the melting temperature and 3HV fraction without any effect on degradation temperature allows the thermal processing of copolymer to melt in the absence of thermal degradation. The melting temperature (T_m) of P(3HB) homopolymer was 178 °C while that of the copolymer (3-hydroxybutyrate-co-3-hydroxyvalerate) (P(3HB-co-3HV)) with a 95 % of 3HV was 108 °C. A minimum value around 75 °C of melting temperature was observed where the crystal lattice transition occurred, at approximately 40 mol % 3HV. For copolymers poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P(3HB-co-4HB)), the T_m value decreases from 178 °C to 150 °C as the 4HB content increases from 0 to 18 % and it is later almost constant in the composition range from 18 to 49 mol % 4HB.

The copolymer P(3HB-co-3HV) is still readily biodegradable even though it has lower crystallinity and better mechanical properties compared to P(3HB). These mechanical properties are decreased stiffness and brittleness, and increased tensile strength and toughness. Besides, P(3HB-co-3HV) has a higher melt viscosity, desirable for extrusion blowing. In contrast, copolymers PHBV poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) have a range of properties which is decided by the composition.

Table 2.2: Properties of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (Rudnik, 2008)



% C6 (hexanoate)	Melting point T_m, °C		Applications
0 (PHB)	180	Hard, brittle, crystalline	
4	150	Hard, some elasticity	moulded articles
6	145	Hard, elastic, flexible	fibres
10	125	Soft, elastic, flexible	films
18	95	Soft, rubbery	coatings

Scientists and industrialists have been finding a substitute for petroleum plastics as it leads to environmental, health, biodiversity and economic problems. A safer type of plastics like the bio-friendly PHB and other member of PHAs family seem to be a possible solution to the problems arising from petroleum plastics. PHAs are biodegradable without any toxicity and bio-evaluable to such an extent that they do not stimulate the human immune system even though the human body can actually degrade the polymer after a period of time. Thus, this meets the demands of numerous medicinal and pharmaceutical applications (Amara, 2008).

As a matter of fact, PHB is produced by microorganisms namely, *Ralstonia eutrophus* or *Bacillus megaterium* in response to the conditions of physiological stress. It can be either produced by pure culture than mixed culture of bacteria. The polymer is mainly a product of carbon assimilation from glucose or starch; in which when there is unavailability of other energy sources, microorganisms employ it as a form of energy storage molecule to be metabolized. Microbial biosynthesis of PHB begins with the condensation of two molecules of acetyl-CoA and subsequently, the reduction of acetoacetyl-CoA to hydroxybutyryl-CoA. Then, the latter compound is made use as a monomer to polymerize PHB (Bugnicourt *et al.*, 2014).

PHAs polymers are thermoplastic and they have different properties, depending on their chemical composition (that is homo-or copolyester containing hydroxyl fatty acids). Some grades of additives PHB are similar to polypropylene (PP) in terms of the material properties and the former have good resistance to moisture and aroma barrier properties. Meanwhile, polyhydroxybutyric acid synthesized from pure PHB is rather brittle and stiff, which mean the elongation at break is typically below 15 % and the *E* modulus is above 1 GPa respectively.

2.3 Polymer Blends

It cannot be denied that polymer blending appears to be an effective method for developing new polymer materials for special applications. This technology is seen as a multi-purpose approach in developing new membrane materials with some modifications were made to their wide range of properties. Polymer researchers show their interest in understanding the evolution of blend morphology when two or more incompatible homo polymers or copolymers are melt-blended in the mixing equipment. In industry, either an internal batch mixer like Banbury mixer (Brabender mixer) or a continuous mixer such as twin-screw extruder (Buss Kneader) is used to conduct melt blending. When two immiscible polymers are compounded in the mixing equipment, there are always two types of blend morphologies specifically, dispersed morphology and co-continuous morphology.

Polymer blending is a convenient way for developing new polymeric materials, which involves the combination of properties of more than one polymer for the reasons that it is usually cheaper and less time-consuming, compared to new monomers and/or new polymerization which needs to be carried out for developing completely new polymeric materials. Regarding polymer blending, it usually takes place in processing machines or those considered as standard industrial equipment like twin-screw extruders. Hence, the financial risk for developing new materials in polymer blends is limited.

The field of manufactured polymer blends, has encountered a gigantic development in size and modernity in the course of recent decades as far as both the logical base and application, compressed in a few distributions. A careful survey of biopolymeric blends and composites and their applications in various industries is likewise accessible. The point of bioartificial mixing is to deliver man-made blends that give novel auxiliary and mechanical properties on the base of the particular properties of common polymers and manufactured polymers. By bioartificial mixing the idea of biomimicry of a few materials can be created and can prompt another era of platforms.

Generally, biopolymers are more costly than engineered polymers. However, natural polymers are plenteous and some might be acquired at a relativity low cost. Typically, high cost is associated with the purification of biopolymers from natural sources. To develop modified materials based on the blends of a natural polymer and a man-made polymer, two components of the mix should be consolidated into one adaptable material. The components can be combined in the molten state (melt mixing) and can be dissolved in the same solvent (Sionkowska, 2011).

A standout amongst the most encouraging strategies solid-phase modification of polymers is the joint action of high pressure and shear deformation on the blend of solid components. Under these conditions, the responding material is subjected to plastic stream with a boundless strain. However, melt-mixing and reaction between solids at high pressures combined with shearing can be dangerous for some biopolymers such as proteins. For example, high pressure and high temperature can lead to denaturation and degradation of such biopolymers. The preparation of a biopolymer blend by dissolution in the same solvent can avoid denaturation of the protein. The issue is that since many naturally occurring polymers are insoluble in common solvents it is necessary to obtain a soluble derivative of natural polymers. Once a water-soluble biopolymer has been accomplished, it is important to choose what sort of synthetic polymer should to be joined with the natural one.

A wide range of material properties that is to be achieved by simply making a change to the blend composition is another advantage of polymer blends. On the negative side, a significant drawback of polymer blends is the difficult recyclability of the materials, which is opposed to neat or just-reinforced resins. Even so, the marketplace for polymer blend-based materials such as automotive, electrical and electronic, packaging, building and household has risen during the past two decades and is believed to rise continuously by 8-10 % in the upcoming decade. The total market for polymer blends is predicted recently to be 1.5 million tonnes per year.

Some investigators examined blend morphology in order to explain the complicated rheological behaviour of two-phase polymer blends whereas other investigators studied that blend morphology is affected by processing conditions (Yu, Dean and Li, 2006). However, there is still no clear picture concerning the evolution of blend morphology during compounding in the mixing equipment. It is not clarified about what conditions under which a dispersed morphology or co-continuous morphology may be formed and whether a co-continuous morphology is stable or unstable intermediate that may eventually be transformed to a dispersed morphology.

In brief, (Koning *et al.*, 1998) stated that, among the factors which affect the evolution of blend morphology during compounding are as follows: (1) temperature, (2) mixing duration in an internal mixer or the residence time in a twin- screw extruder, (3) mixing intensity (rotor speed in an internal mixer or screw speed in a twin-screw extruder), (4) blend composition, (5) viscosity ratio, (6) elasticity ratio and (7) interfacial tension.

Polymer blends is related to the mixture of at least two types of polymer that blends together to create a new material with desired physical properties. The polymer blends commonly divided into three categories (Shah *et al.*, 2008):

i. Miscible polymer blends (homogeneous polymer blend): Polymer blends that having a single-phase structure. One of the properties of the polymer is having one glass transition temperature. Example of miscible polymer blends are:
    a) Homopolymer–copolymer: Polypropylene (PP) – EPDM and Polycarbonate (PC) – Acrylonitrile butadiene styrene (ABS)
    b) Homopolymer-homopolymer: Polyethylene terephthalate (PET) – Polybutylene terephthalate (PBT) and Poly (methyl methacrylate) (PMMA) – Polyvinylidene fluoride (PVDF).
ii. Immiscible polymer blends also called as heterogeneous polymer blends. The blends exhibit two glass transition temperatures and immiscible blends between two components of the polymer.
iii. Compatible polymer blends that are immiscible polymer blends and show uniform microscopically physical properties. (Dunford, 2012) stated that macroscopically uniform properties caused by sufficiently strong interaction between the component polymers.