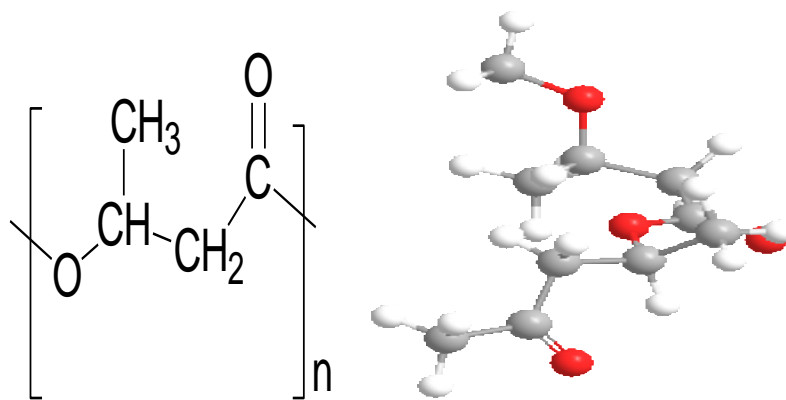


**CHAPTER TWO**  
**LITERATURE REVIEW**

## 2.0 Literature review

### 2.1 Introduction

Polymer materials are created by a long repeating series of smaller molecules (chains of smaller molecules). Poly(3-hydroxybutyric acid) (PHB) has attracted much commercial interest as a plastic and biodegradable material because some its physical properties are similar to those of polypropylene (PP), even though the two polymers have quite different chemical structures. PHB exhibits a high degree of crystallinity, has a high melting point of approximately 180 °C and most importantly unlike PP. PHB is rapidly biodegradable. **Figure 2.1** shows the structure of PHB.



**Figure 2.1:** Structure of poly(3-hydroxybutyrate).

Two major factors which currently inhibit the widespread use of PHB are its high cost and poor mechanical properties. The production costs of PHB are significantly higher than for plastics produced from petrochemical resources, and its stiff and brittle nature makes processing difficult and impedes its ability to handle high impact. Improvement of thermal properties of biodegradable poly(3-hydroxybutyric acid) (PHB) modification with Acryloyloxyethyl Isocyanate (Chen *et al.*, 2012).

## **2.2 Polyhydroxyalkanoates (PHAs)**

Polyhydroxyalkanoates (PHAs) are polyesters produced by numerous bacteria in nature that act as intracellular reserves of carbon or energy. PHAs are generally biodegradable and have good biocompatibility, that makes them attractive as biomaterials (Bruzaud, 2014). Many PHA monomer structures have been reported. The occurrence of PHAs in bacteria has been known since 1920s, when Lemoigne reported the formation of poly(3-hydroxybutyrate) (PHB) inside bacteria. PHAs are synthesized from many living organisms biochemically through microbial fermentation or maybe produced by transgenic plants. PHAs are naturally occurring semi-crystalline polymers found in microorganisms such as bacteria and fungi. They are well known kind of thermoplastic aliphatic polyester, which show material properties that are similar to polypropylene. The main advantages of these materials over petrochemical plastics are that they are from a natural, renewable source as well as biodegradable. It can be degraded to water and carbon dioxide under environmental conditions by a variety of bacteria (Chiellini & Solaro, 1996).

PHAs are thermoplastic, biodegradable, biocompatible, and nontoxic. In terms of fabricability, they scarcely differ from plastics based on petrochemical raw materials so that the installations customarily used in plastics technology are also suitable for fabrication of PHAs. Because of their biodegradability and biotechnical production from biogenic raw materials, PHAs are considered alternatives to non-degradable polymers based on fossil-derived raw materials. The main candidates for the large-scale production of PHAs are plants and bacteria. Accumulating PHAs is a natural way for bacteria to store carbon and energy, when nutrient supplies are imbalanced. As PHAs are insoluble in water, the polymers are accumulated in intracellular granules inside the cells. The activities of these enzymes may vary and depend on the composition of the polymer and the environmental conditions. PHAs have much potential applications of

medical materials such as absorbable surgical sutures, matrices for drug delivery systems and as biodegradable molded plastics (Ha & Cho, 2002).

### **2.3 Poly(3-hydroxybutyrate) (PHB)**

PHB was one of the most commonly studied polymers since its early introduction in the 1920s (Verhoogt *et al.*, 1994; Chiellini & Solaro, 2003; Khanna & Srivastava, 2005; Wada *et al.*, 2007). PHB is one type of polyhydroxyalkanoate often used as a biomedical material due to its biodegradable and biocompatible nature. However, the mechanical and thermal properties of PHB must be improved before it can be used in a wider variety of biomedical applications (Reddy *et al.*, 2003).

The best studied polymer within the PHA family is poly(3-hydroxybutyrate) (PHB), which has a model character for research on PHA and for establishing and optimizing biotechnical PHA production processes. The properties of PHB (brittleness, stiffness), however, are not optimal for many applications; for them, rather, other PHA with more favorable properties come under consideration (Zinn *et al.*, 2001).

The blending of friendly environmental biopolymers with industrial synthetic polymers were a standpoint tool to produce novel materials with combined features in having both improved application properties and low price advantages in material performance (Bonartsev *et al.*, 2007). Different techniques have been used to study PHB by gas chromatography/Mass spectrometry and observed degraded PHB films by SEM (Gonzalez *et al.*, 2005). PHB polymers are a biodegradable thermoplastic polymer. Its production cost might be developing genetic engineering skills. Because PHB is prone to thermal degradation and very brittle, it is essential to develop its mechanical properties and process ability through blending or copolymerization. There were been numbers reports on the blending of PHB with other polymers or biodegradable polymers that are recalcitrant to biodegradation (Kim, Lee, *et al.*, 1999). One way to reduce the amount of plastic residue was the use of biodegradable materials which

obtained through renewable resources and contribute to the geochemical cycle (Savenkova *et al.*, 2000; Rosa *et al.*, 2004; Bucci *et al.*, 2007).

The multidistributed characteristics of polymer systems present a huge challenge to the analyst. Infrared spectrometry had proved to be a superior tool in polymer analysis, but was severely narrow by the multicomponent nature of polymer samples. Traditional sample fractionation followed by FTIR analysis could yield results but was very costly on terms of time and effort (Dwyer & Zhou, 2011).

Biodegradable polymers had been the subject of great deal of research, with the ultimate aim of producing physically and economically viable commercial materials (Moore & Saunders, 1998). In recent times, PHB obtained via plants, but in old times it is obtained via fermentation, is biodegradable (Mousavioun, 2011).

It is to imagine that the incorporation of PVAc different proportion into PHB will produce useful polymers for a wide range of application. Biodegradable polymers had been the primary consideration in the development materials due to problems associated and had been formulated for uses such as sutures, drug delivery devices, vascular grafts, artificial skin and others (Mark, 2007).

PHB, one of the most important biodegradable polymers, is well-known for its satisfactory mechanical properties, similar to those of polypropylene (PP). It provides a better carbon dioxide barrier than PP or PE and a reasonable water barrier, better than (Nylon 6.6) polycaprolactone as well as good resistance to solubility in water (Gonzalez *et al.*, 2005; Parra *et al.*, 2011).

There had been many reports on the blending of PHB with other biodegradable or nonbiodegradable polymers; these include poly(epichlorohydrin) (PECH) (Paglia *et al.*, 1993; Kim, Shin, *et al.*, 1999; Yu *et al.*, 2006; Yu, 2009), poly(vinyl alcohol) (PVA) (Azuma *et al.*, 1992), atactic poly-[(R,S)-3-hydroxybutyrate] and its block copolymer

with poly(ethylene glycol) (PEG) (Kumagai & Doi, 1993), Poly(ethylene-co-vinyl acetate) or poly(ethylene oxide) (Kim, Lee, *et al.*, 1999), chitosan (Ikejima *et al.*, 1999) and the crystallization behavior and phase structure of PHB/chitosan studied (Ikejima & Inoue, 2000; Cheung *et al.*, 2002).

Immiscible blends had been prepared by mixing PHB with poly(1,4-butylene adipate)(PBA) (Kumagai & Doi, 1992), Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (Verhoogt *et al.*, 1994; Avella *et al.*, 2000), with cellulose derivatives (cellulose–acetate–butyrate and cellulose–acetate–propionate) (Buchanan *et al.*, 1992; Lotti *et al.*, 1993).

Biodegradation of polyhydroxyalkanoates is reliant on the presence of depolymerase enzymes; these initiate the biodegradation pathway. Therefore PHA should be biodegradable in most environments. Blends of PHA with other biodegradable polymers also usually show improved biodegradability when compared with pure PHAs (Verhoogt *et al.*, 1994). PHBV had a higher rate of biodegradation than PHB; probably due to the reduction in crystallinity (Moore & Saunders, 1998).

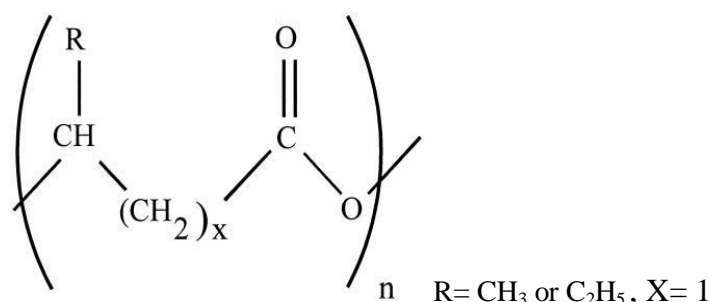
Poly(3-hydroxybutyrate) was a biodegradable produced by microorganisms under nutrient limitation conditions (Araujo *et al.*, 2011). Biodegradable PLA-PHB blends had been successfully prepared by melt mixing PLA, PHB and a new type of plasticizer (Abdelwahab *et al.*, 2012).

Polymer blend means a mixture of at least two polymers or copolymer, comprise more than 2wt% of each component (Utracki, 2000). Natural polymers have been widely investigated as biotechnological resources because of their unique properties, for example, degradability, and biological compatibility (Peesan *et al.*, 2003). The main setback of PHB when used as a thermoplastic is its thermal instability during melt processing. Therefore, intense interest has been shown in the thermal degradation of

PHB and other related poly (hydroxyalkanoate)s. Recently, it has been demonstrated that PHB is a chemically recyclable material with end products such as crotonic acid, linear oligomers having a crotonate end group (Morikawa & Marchessault, 1981; Ariffin *et al.*, 2008).

## 2.4 Microbial polyesters

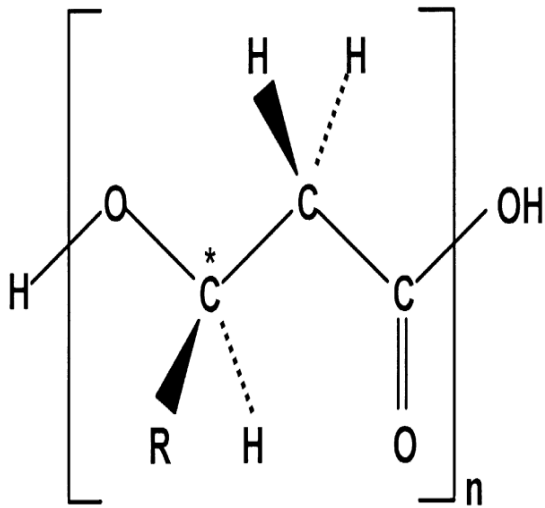
Polyhydroxyalkanoates (PHAs) are arguably the most well researched group of biodegradable plastics and their basic structure is shown in **Figure 2.2**.



**Figure 2.2:** Structure of polyhydroxyalkanoate PHA (Reddy *et al.*, 2003; Sood, 2010). Both PLA and PHB were biodegradable polyesters and were used in consumer products by several industrial sectors due to their biocompatibility, biodegradability and sustainability (Abdelwahab *et al.*, 2012). PHB had the biodegradability biocompatibility. Unfortunately, they present the draw-backs of a poor thermostability and a relatively low impact resistance. Certainly, above 170 °C these polyesters undergo a reduction of molecular weight proportional to the time. The mechanism of the thermal degradation follows a random scission at the ester groups according to a  $\beta$ -hydrogen elimination. Generally, Polymer from renewable resources have been attracting ever-increasing attention over the past two decades, can sometimes be classified according to their physical character and can be classified into three groups: first natural polymers such as cellulose, starch and protein; second synthetic polymers from bioderived monomers such as Polylactic acid (PLA); and third polymers from microbial fermentation such as polyhydroxybutyrate, wide ranges of naturally occurring polymers





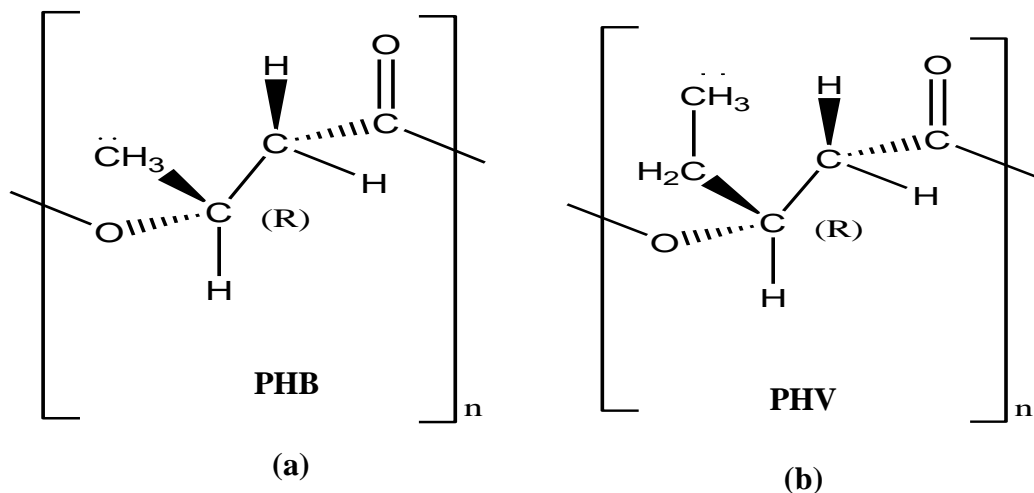


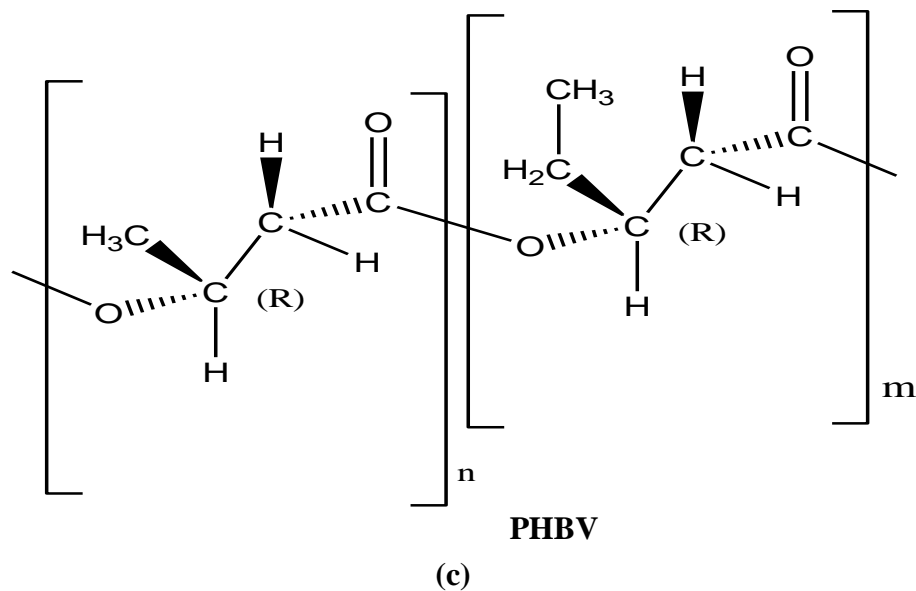
**Figure 2.4:** Chemical structure of poly(3-hydroxybutyrate) (PHB) and medium chain length poly(3-hydroxyalkanoate) (mclPHA).

All monomers have one chiral center (\*) in the *R* position. Poly(3-hydroxybutyrate): $R=CH_3$ ; poly(3-hydroxyvalerate): $R=C_2H_5$ ; mclPHA:  $R=C_3H_7 - C_{11}H_{25}$ ,  $N=100-30\ 000$  monomers (Zinn *et al.*, 2001).

PHB is probably the most common type of PHA, but many isolation of this class are produced by a variety of organisms: these include poly (4-hydroxybutyrate) (P4HB), polyhydroxyvalerate (PHV), polyhydroxyhexanoate (PHH), polyhydroxyoctanoate (PHO), and their copolymers (Khanna & Srivastava, 2005). The structure are shown in

**Figure 2.5.**





**Figure 2.5:** Chemical structures of (a) PHB, (b) PHV and (c) their copolymer PHBV (Bugnicourt *et al.*, 2014).

PHB is poly-(R)-3-hydroxybutyric acid, PHB was such a fully biodegradable, thermoplastic aliphatic polyester, produced by a wide variety of bacteria the most abundant natural polymer (polyester). The most important sources of PHB today are bacteria from cheap renewable raw materials (Achilias *et al.*, 2011).

Thus, several modifications had been proposed to improve their processing and mechanical properties, which include the preparation of copolymers containing monomeric units derived from hydroxyl alcanoic acids and blending these with PLA and PHB (Abdelwahab *et al.*, 2012). PHB was microbial polyesters presenting the advantages of biodegradability and biocompatibility over other thermoplastics with useful mechanical properties (Avella *et al.*, 2000). Hitherto, there were many references to attempts to mix PHB with other polymers with the aim of improving its mechanical properties, unfortunately with only limited success up until now. Under the term polymer blends, the physical characteristics for two compatible or incompatible polymer components will be explained. The aim is to develop a new material with better mechanical properties, which cannot achieve with homo or copolymer alone. For incompatible polymer blends the material passes a phase separation with bad adhesion

at the boundary surfaces and two-glass transition temperature. For compatible polymer blends the material has one glass transition temperature. PHB is the only polymer from the group of PHA's, which is produced, in large quantities. This polymer has poor mechanical properties. In order to solve this problem by biologists, chemists Engineers or physicists:

It must develop new microbes to be able to produce the copolymer by variation of the food composition. Unfortunately the copolymer is manufactured in limited quantities and it is too brittle like PHB. The chemist controls the molecular weight during the polymerization to improve the mechanical characteristics. Fortunately the bacteria make the polymerization alone. For the Engineering point view, PHB possess badly processable. It sticks on metal surface and thermal unstably. For the physical point of view, the reasons for the brittleness of PHB are known, until today there is no accurate elimination. Solves this problem by a new blends and new results achieve in polymer physics and applications in polymer science. PHB is fully biodegradable polyester with optical activity, piezoelectricity, and very good barrier properties. PHB is a partially crystalline material with a high melting temperature.

### **2.5.2 Properties of PHB**

PHB is a thermoplastic with a great potential owing to its biodegradability, bioreabsorbation and biological synthesis from a renewable source, belonging to the family of polyhydroxyalkanoate PHAs (Antunes & Felisberti, 2005). It has physical and mechanical properties comparable to those of isotactic polypropylene (ipp). Therefore during processing it flows easily. It is not water soluble but is 100% biodegradable. PHB is homopolymer, it has a high melting point, a high degree of crystallinity. It degrades at temperatures around its melting point. Therefore has a narrow thermal processing window.

PHB has low permeability for O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>. PHB has the disadvantage; it has a high cost and thermally unstable during processing therefore the viscosity and molar mass decrease. A remarkable characteristic of PHB is a brittle, stiff material and pure homopolymer. The degree of brittleness depends on the degree of crystallinity, glass temperature and microstructure. At room temperature, the longer it is stored the more brittle it becomes. PHB does not contain any residues of catalysts like other synthetic polymers. PHB is perfectly isotactic and does not include any chain branching like, for instance Polyethylene (PE). Its melting temperature is 170-180 °C and highly crystalline with crystallinity above 50 % and glass transition temperature is approximately of 55 °C (Khanna & Srivastava, 2005).

PHB was observed to have properties similar to those of PP, PHB is a high molecular weight energy storage product of bacteria and algae, with a high degree of crystallinity. It was found to be brittle when held at ambient temperatures for more than a couple of days and has poor chemical resistance (Moore & Saunders, 1998). Characterization of pure PHB was carried out. As reported in the literature, it was found that PHB is a highly crystalline, biodegradable polymer with a melting temperature of 176 °C. It forms large spherulites with cracks and splits at the spherulite boundaries, and hence it is brittle. It has poor thermal stability due to chain scission, which occurs at a temperature slightly higher than its melting temperature. PHB shows poor thermal stability at temperature above the melting point (Grassie *et al.*, 1984; Kopinke *et al.*, 1996; Aoyagi *et al.*, 2002; Hablot *et al.*, 2008).

It exhibits poor processability due to its extremely low melt viscosity. Its melt viscosity decreases with the increasing processing time and temperature. However, PHB has poor mechanical properties and is difficult to process. The main reasons for its poor properties include low T<sub>g</sub>, undergoes secondary crystallization which occurs during

storage at ambient temperature, and has a low nucleation density which allows large spherulites (Zhang, 2011).

### **2.5.2.1 Physical and Chemical properties**

PHB is a linear saturated polyester, non-toxic and is soluble in almost a polar solvent such as chloroform, other chlorinated hydrocarbons and insoluble in water. This differentiates PHB from most other currently available biodegradable plastics, which are either water soluble or moisture sensitive (Avella *et al.*, 2000; Reddy *et al.*, 2003).

PHB is the only polymer from the group of PHA's to be produced in large quantities and possesses very good barrier properties (Doi *et al.*, 1992). Pure PHB has some disadvantages, such as its high degree of crystallinity and its thermal instability and has good barrier properties such as PVC and poly(ethylene terephthalate)(PET) and can be used in packaging industries as a biodegradable plastic for solving environmental pollution problems. Therefore, its mixture with conventional polymers with low degradability but good mechanical properties can be a solution to obtain environmentally more friendly biodegradable polymers (Kawamura *et al.*, 2002).

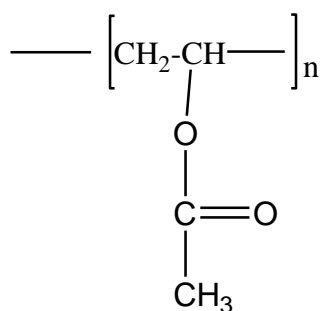
It is tensile strength of 40 MPa, which is close to that of PP and good oxygen permeability. It is a good UV resistant, but poor resistance to acids and bases.

### **2.5.2.2 Biological properties**

PHB is a non-toxic, natural product. Therefore it can play a role in various medical applications such as compatible with the blood and tissues of mammals, a normal metabolic in the human blood. As the body reabsorb PHB it might be used as a surgical implant, in surgery, as seam threads for the healing of wounds and blood vessels, and therefore it can play in the pharmacology applications such as microcapsules in therapy or as materials for the cell and tablet packaging. Therefore, it can be applied in the food industry for example, bottles, laminated foils, fishnets, potted flower, hygiene, fast food, one-way cups, agricultural foils and fibers in textile.

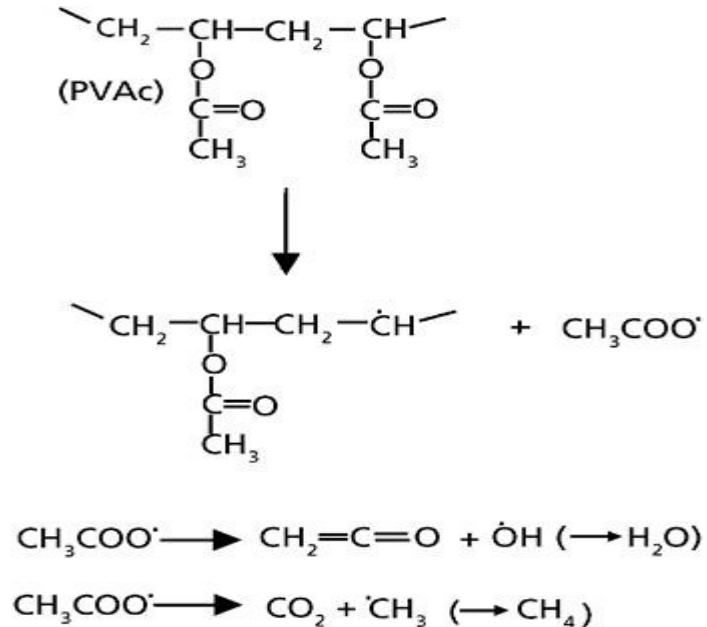
### 2.5.3 Properties of PVAc

Poly(vinyl acetate) (PVAc) is a rubbery synthetic polymer with the formula  $(C_4H_6O_2)_n$ . It belongs to the polyvinyl esters family with the general formula  $[RCOOCHCH_2]$ . It is a type of thermoplastic and it is used primarily in adhesives, both emulsion and hot melt types. It is also used in water based emulsion paints. It has an amorphous density at 25 °C around  $1.19 \text{ g cm}^{-3}$ , glass transition temperature around 30 °C and molecular weight of repeat unit around  $86.09 \text{ g mol}^{-1}$ . Polyvinyl acetate (PVAc), a synthetic resin prepared by the polymerization of vinyl acetate. In its most important application, polyvinyl acetate serves as the film-forming ingredient in water-based (latex) paints; it also is used in adhesives. Vinyl acetate ( $CH_2=CHO_2CCH_3$ ) is prepared from ethylene by reaction with oxygen and acetic acid over a palladium catalyst. Under the action of free-radical initiators, vinyl acetate monomers can be linked into long, branched polymers (large, multiple-unit molecules), in which the structure of the vinyl acetate repeating units is:



**Figure 2.6:** Structural of polyvinyl acetate.

PVAc polyblends mechanism radical degradation. The mechanism for the formation of acetate radicals as shown in **Figure 2.7**, provides an explanation for the production of side volatiles ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , methane and ketene) in the degradation of PVAc (Jamieson & McNeill, 1976; Zulfiqar & Ahmad, 2001).



**Figure 2.7:** Free-radical mechanisms of thermal degradation in PVAc

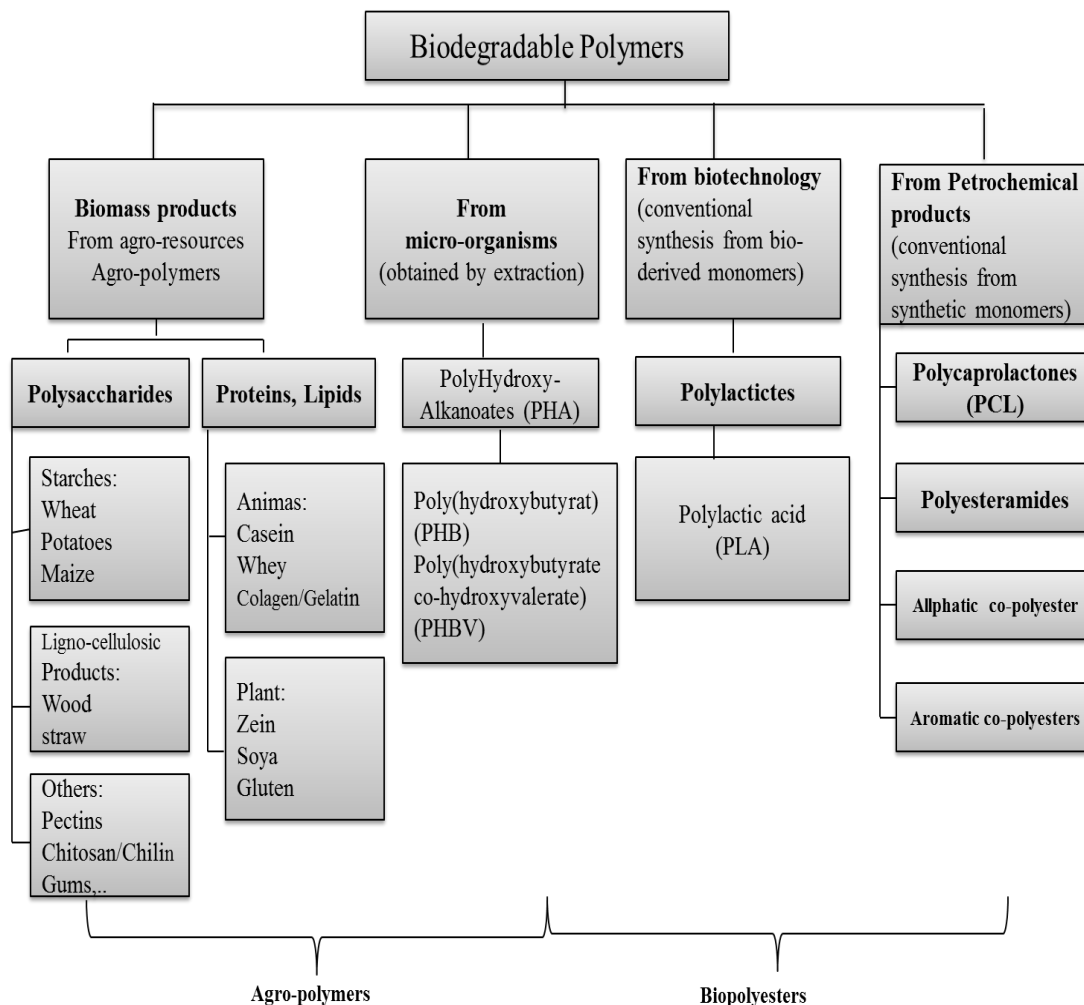
#### 2.5.4 Some application of PHB:

PHB originates from renewable sources was a biodegradable aliphatic polyester. It degraded completely by aerobic microorganisms to CO<sub>2</sub> and H<sub>2</sub>O (Duarte *et al.*, 2006; Dias *et al.*, 2009). PHB is miscible with poly(ethylene oxide) (El-Shafee *et al.*, 2001), poly(methyl methacrylate) (An *et al.*, 2000), Poly(vinyl phenol) (Iriando *et al.*, 1995; Xing *et al.*, 1997), poly(vinylidene fluoride) (Chiu *et al.*, 2001; Kaito, 2006), Cellulose acetate butyrate blends (Buchanan *et al.*, 1992; Lotti *et al.*, 1993; El-Shafee *et al.*, 2001) (Paglia *et al.*, 1993; Sadocco *et al.*, 1993; Shafee, 2002; de Lima & Felisberti, 2006) poly(ethylene-co-vinyl acetate) or poly(ethylene oxide) blends (Kim, Lee, *et al.*, 1999), poly(epichlorohydrin-co-ethylene oxide) (PECH-EO) (Zhang *et al.*, 2000), poly(vinylidene chloride-co-acrylonitrile) (Gonzalez *et al.*, 2002), poly(cyclohexylmethacrylate) (Lotti *et al.*, 1993), poly(butylene succinate) (Qiu *et al.*, 2003), poly( $\gamma$ -benzyl-L-glutamate)(Deng *et al.*, 2001), poly(butylene succinate-co-butylene adipate) and poly (butylenesuccinate-co- $\epsilon$ -caprolactone) (He *et al.*, 2000), Poly(vinyl acetate-co-vinyl alcohol) (Xing *et al.*, 1998), poly(vinyl alcohol) (Azuma *et al.*, 1992; Iriando *et al.*, 1995; Huang *et al.*, 2005). PHB is biodegradable with polyaniline (Araujo *et al.*, 2011), poly(ethylene-co-vinyl acetate) (Avella & Martuscelli, 1988; Choi *et al.*, 1995; Kim, Lee, *et al.*, 1999), Poly(Ethyleneglycol) (Parra *et al.*, 2011), grafted with vinyl acetate (Wada *et al.*, 2007), studied the thermal behaviour and crystallinity of PHB with poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); P(HB-co-HHx) (Murakami *et al.*). PHB is blending with poly( $\epsilon$ -caprolactone) (Antunes & Felisberti, 2005), PHB/lignin (Mousavioun *et al.*, 2010; Mousavioun *et al.*, 2013).

Biodegradable polymers consists two groups and four different families, first group it's the main the agro polymers [polysaccharides] and second group biopolymers (biodegradable polymers). Biodegradable polymers show a large range of properties and



compete with non biodegradable thermoplastics in different fields (biomedical, packaging, etc.)(Avérous, 2004; Ebnesajjad, 2012).



**Figure 2.8:**Classification of the biodegradable polymers (Ebnesajjad, 2013).

Its copolymers, polyhydroxyalkanoate (PHA), are completely biodegradable under anaerobic and aerobic conditions and can be produced from renewable resources. They are biologically synthesized polyesters produced by a number of microorganisms and are consequently subjected to degradation by bacteria in the soil (Murakami *et al.*).

Biodegradable plastics are an attractive route to environmental waste management and can replace conventional polymers when recovery for recycling or incineration is difficult and/or not cost-effective. Research has focused on both the addition of biodegradable polymers to common thermoplastics and on purely biodegradable, natural and synthetic polymers (Verhoogt *et al.*, 1994; Park *et al.*, 2001).

New plastic properties can be achieved by blending of PHA with other polymers and there is much lactate activity in this field (Scandola *et al.*, 1997; Tighe *et al.*, 1997; Zhang *et al.*, 1997c; 1997b; Zhang *et al.*, 1997a). Often the mixture changes the crystallinity of the plastic and the crystallization rate and finally also the mechanical properties of the material. Thus, a mixture of 40– 60 % of polycaprolactone (PCL) in PHB improved the mechanical properties over P(HB-co-HV). A 40 % PCL and 60 % PHB mixture had a decreased oxygen permeability that was only 5% that of polyethylene (Urakami *et al.*, 2000).

Maekawa and coworkers reported that blends of PHB and cellulose propionate were completely miscible since they had a single glass transition, a depression in the equilibrium melting temperature of PHB and a decrease in the spherulitic growth rate of the PHB component. Also the tensile strength was better for the blend PHB/cellulose propionate than for PHB only. However, not all blends are compatible. For example, PHB and poly(L-lactide) (PLLA) form a compatible mixture only when the molecular weight of PLLA is smaller than 11 700 Da (Yoon *et al.*, 2000). Another approach to modify the chemical properties of PHB is the addition of plasticizers. These low molecular weight compounds give the plastic a better ductility (Hobbs & Barham, 1997; Yoshie *et al.*, 2000). However, plasticizers may significantly alter the biodegradation of the polymer, as shown by Laprol (Savenkova *et al.*, 2000) or with time the plastic becomes brittle due to leaching of the plasticizer (Zinn *et al.*, 2001).

In medicine, PHB is compatible with the blood and tissues of mammals. The monomer of PHB is a normal metabolic in the human blood. As the body reabsorbs, PHB it might be used as a surgical implant, in surgery, as seam threads for the healing of wounds and blood vessels.

## **2.6 Blends of PHB**

### **2.6.1 Introduction**

Blending of polymers cause compatibility among components has a marked influence on the resulting physical properties of polymer blend and blending of polymers are an important process for developing industrial applications of polymeric materials (Peesan *et al.*, 2003).

Polymer blend is defined as a mixture of at least two macromolecular substances, polymers or copolymers, in which the ingredient content is above two weight percent.

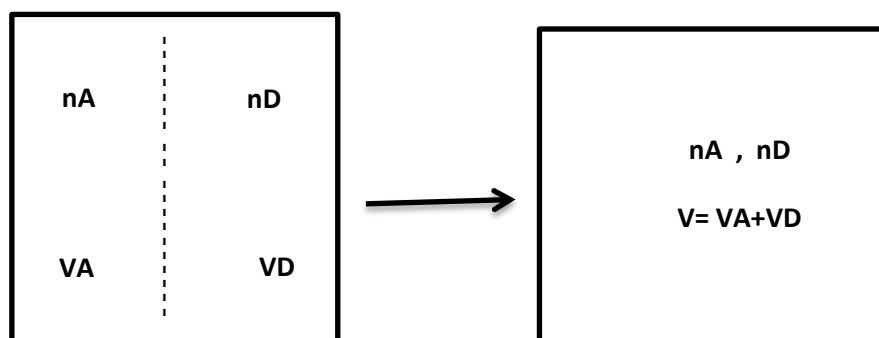
Reasons for Blending:

1. Developing materials with a full set of desired properties.
2. Extending engineering resins' performance by diluting them with low-cost commodity plastics.
3. Improving specific property.

Only a few studies on the amorphous–crystalline polymer blends have been reported but the amorphous-amorphous polymer blends have been the subjects of numerous studies in the past (Yingkang *et al.*, 1985). Polymer blends by definition are physical mixtures of structurally different homopolymers or copolymers. In equilibrium, a mixture of two polymers in the amorphous phase may exist as a single phase of intimately mixed segments of the two components. Such a blend is homogeneous on a microscopic scale and is considered to be miscible in the thermodynamic sense. When a mixture of two polymers separates into two distinct phases consisting primarily of the individual components, the blend is heterogeneous on the microscopic scale and is considered to be immiscible in the thermodynamic sense (Mukerji, 1980; Verhoogt *et al.*, 1994).

On the other hand, blending of PHB may decrease the  $T_m$ , which implies the possibility of processing the materials at a lower temperature to avoid or limit degradation (Avella *et al.*, 2000).

Many researchers have studied polymer blending for the development of new materials and to tailor properties of the blends by exploiting the physical, chemical, mechanical and thermal properties of the individual components. There are several theories that have been developed to describe compatibility and miscibility of polymers. One of the most famous is the Flory-Huggins treatment of polymer/solvent interactions in binary polymer systems. This theory provides a basic understanding of the occurrence of different types of phase diagrams independent of temperature and molecular weight. **Figure 2.10** illustrates the process of mixing two polymers, A and D; where  $n_A$  and  $n_D$  are moles of the polymers A and D, and  $V_A$  and  $V_D$  are their respective volumes, with  $V$  being the total volume.



**Figure.2.9:** The description of the process for mixing two polymers (Strobl, 2007).

### 2.6.2 Preparation of PHB blended solutions and films

Polymer blending is considered to be one of the most effective methods for lowering the cost of production of these types of polymers, and in certain cases improves processing and product quality (Mousavioun *et al.*, 2013). Mostly, there are main methods that are commonly used in the blending of PHB such as use chloroform to dissolving by evaporation (solution blending) and mixing under fusion conditions (blending). Therefore, according to the literature, solution blending is the most applied method for

preparing PHB due to its simplicity and suitability for producing various forms of blends (fibers, beads, microspheres and film) (Mousavioun *et al.*, 2010).

The PHB homopolymer is a biodegradable, biocompatible thermoplastic, implying that it is a resin that becomes highly viscous and moldable at temperatures close to or above its melting point ( $T_m$ ). Its properties are often compared to those of polypropylene, as both polymers have similar  $T_m$ , degrees of crystallinity, and glass transition temperatures ( $T_g$ ). However, PHB is both stiffer and more brittle than polypropylene. The brittleness of PHB is largely due to the presence of large crystallinities in the form of spherulites, which form upon cooling from the melt (Avella *et al.*, 2000).

### **2.6.3 Blended of PHB with synthetic polymers**

Synthetic polymers are widely used in biomedical implants and devices because they can be fabricated into various shapes.

### **2.6.4 Blending of PHB with natural polymers**

In addition, PHB blends with starch acetate (SA), and found the PHB/SA blends were immiscible. Melting temperatures of PHB in the blends showed some shift an increase of SA content. Melting enthalpy of the PHB phase in the blend was close to the value for pure PHB. FTIR absorptions of hydroxyl groups of SA and carbonyl groups of PHB in the blends were found to be independent of the second component at  $3470\text{ cm}^{-1}$  and  $1724\text{ cm}^{-1}$ , respectively (Zhang *et al.*, 1997c; Thomas *et al.*, 2012).

Biodegradable plastics are an attractive route to environmental waste management and can replace conventional polymers when recovery for recycling or incineration is difficult and/or not cost-effective. Research has focused on both the addition of biodegradable polymers to common thermoplastics and on purely biodegradable, natural and synthetic polymers. Among these, poly (3-hydroxybutyric acid) (PHB), has been developed and investigated as one of the potential candidates for biodegradable

plastics to reduce pollution caused by synthetic polymer waste. PHB, a saturated linear polyester behaving like a conventional thermoplastic material, is a polymer of poly(3-hydroxybutyric acid) produced via biosynthesis by a wide variety of bacteria. PHB serves as an intracellular storage material for carbon and energy and is accumulated as granules within the cytoplasm of the bacteria (Verhoogt *et al.*, 1994; Park *et al.*, 2001).

#### **2.6.5 Poly(3-hydroxybutyric acid) and a modified natural biodegradable polymer**

**PHB-fiber composites:** Addition of wood cellulose fibers to PHB improves its stiffness and strength but also increases brittleness (Gatenholm *et al.*, 1992). The addition of HV units (6, 10 or 15 %) to PHB results in composites with increased elongation at break and improved ductility. Cellulose fibers do not influence PHA crystallinity, but restrict the mobility of the chain segments in the amorphous phase.

**PHB-cellulose ester blends:** Miscibility was observed for blends of PHB with cellulose acetate butyrate (CAB) and hydroxyl cellulose acetate (HECA) (Zhang *et al.*, 1997b) and cellulose acetate propionate (CAP) (Scandola *et al.*, 1992). These transparent blends are stable homogeneous amorphous glasses, showing a single  $T_g$  which decreases linearly with increasing PHB content in excellent agreement with the behavior of miscible.

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