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Manufacturing and properties of PHB

1.1 Introduction

The amount of plastic waste increases every year and the exact time needed for its biodegradation is unknown. Nowadays plastics and synthetic polymers are mainly produced using petrochemical materials that cannot be decomposed. Therefore they contribute to environmental pollution and are a danger to many animals. During the last decade, much attention has been focused on the production of bacterial polyesters. Different bacterial types [1-7] of microorganisms produce PHB from renewable sources from sugar and molasses as intracellular storage materials. Lemoigne [1] discovered PHB in 1925 from Bacillus megaterium. The chemical structure of PHB is

\[-\left\{ O - CH(CH_3) - CH_2 - ( C = O ) \right\}_n -\]

PHB is a fully biodegradable polyester with optical activity, piezoelectricity, and very good barrier properties [6,8]. PHB is a partially crystalline material with a high melting temperature and a high degree of crystallinity. PHB is a thermoplastic, belonging to the family of polyhydroxyalkanoate PHAs. It has physical- and mechanical properties comparable to those of isotactic polypropylene iPP [4]. PHB is stiff and brittle. 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 PE. Therefore during processing it flows easily. It is not water-soluble but is 100 % biodegradable. PHB has low permeable for O2, H2O and CO2 [6,8].

PHB has disadvantage: it has high cost and thermally unstable during processing, therefore the viscosity and molar mass decrease (see 4).

1.2 Possible applications

1) 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.
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(1) In pharmacology, PHB can be used as microcapsules in therapy or as materials for cell and tablet packaging.

(2) In packaging for deep drawing articles in the food industry, for example, bottles, laminated foils, fishnets, potted flower, hygiene, fast food, one-way cups, agricultural foils and fibres in textile.

1.3 Problem description

Nowadays, plastics and synthetic polymers are mainly produced from petrol chemical elements, which do not decompose, thus resulting in environmental pollution. They are stored, burnt or recycled. During combustion, water and carbon dioxide are released into the atmosphere, i.e., an increase in the carbon dioxide concentration in the atmosphere occurs. By recycling polymers, the material quality decreases. Biological polymers are part of a cycle, i.e., water and carbon dioxide are used during the photosynthesis in the plant. The bacteria use carbohydrates by fermentation in the manufacture of PHB. In the USA, Europe and Japan it is expected that biodegradable materials will be important due to their material properties being suitable for a wide range of fields. Waste is currently causing serious environmental problems in many countries, especially in industrialised countries. In household waste 30 percent are all types of packaging foil, i.e., packaging foils for foods, bags and coated foil on paper. To solve these problems, we should use environmentally friendly foils (blends) and favors biodegradation on the compost keep instead of burning. Blends can be made and can be used instead of PP, PE and PVC foil.

1.4 Manufacture of PHB

The manufacturing process of PHB begins with sunlight. Through photosynthesis carbon dioxide from the atmosphere is converted to carbohydrates via sugar beets or sugar cane. These carbohydrates are the raw material for the manufacture of PHB. PHB can be produced from glucose as a raw material or agricultural waste like, for instance, molasses or material, which is refined from the processing of sugar beets and lactose. The sugar splits up in the metabolism to C\textsubscript{2} building blocks, which are converted, over several steps, to C\textsubscript{4} monomers. Finally, PHB is polymerized. The biosynthesis pathway of PHB is shown in the figure (1.1). The fermentation process (see figure 1.2) is carried out in two steps:

(1) Selected bacteria are used for prefermentation; the cells are grown at 30°C in a stream of air in a mineral medium with glucose as a carbon-source. The cells multiply after 24 hours and reach approximately a cell density of 20g/l. This is called prefermentation.
(2) The cells continue to multiply and after 40-80 hours reach a cell density of 100 g/l. PHB occurs as discrete granules with diameters of (0.3-1 µm) in cells as storage material. At the end of the fermentation process, the cell has a dry mass 80% in the form of PHB. For 1 kg PHB: approximately 2.8 kg of sugar are needed.

**There are two isolation processes:**

(1) The extraction method: mechanical loads destroy the cells’ walls and then the polymer is solved in chloroform or another solvent like methyl chloride, 1,2-dichloroethane, pyridine and propylene carbonate. The remains of the cell must be separated by centrifugation and filtration of the solvent.

(2) Enzymatic method: enzymes at 37°C destroy the cell wall.

![Biosynthetic pathway of PHB from acetyl-CoA.](image)

**Figure 1.1**: Biosynthetic pathway of PHB from acetyl-CoA.
Figure 1.2: The life cycle of PHB is a cycle process.
1.5 The hitherto exiting science and technology in this field

PHB is the only polymer from the group of PHA’s to be produced in large quantities. This polymer has poor mechanical properties [9,8,9,10]. PHB is a partially crystalline material [2], has good barrier properties such as PVC and PET [8] and can be used in packaging industries as a biodegradable plastic for solving environmental pollution problems. There are 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 [14]. Most polymers cannot be mixed from a thermodynamic point of view. The chemical incompatibility does not permit a good mixture, i.e., there is no good distribution in other polymers. There are many references to miscible blends containing PHB. PHB is miscible with poly(ethylene oxide) [15-19], poly(vinylidene fluoride) [20,21], poly(vinyl acetate) [22,23], poly(epichlorohydrin) [24-26], poly(methyl methacrylate) [27-30], poly(vinyl phenol) [31,32], poly(vinyl idene chloride-co-acrylonitrile) [33], and poly(epichlorohydrin-co ethylene oxide) [34] and poly(cyclohexylmeth acrylate) [27]. PHB is to a certain extent miscible with ethylene-propylene rubber [22,35], ethylene-vinyl acetate copolymer [36], poly(vinyl alcohol) (37,38), poly(L-lactid) [39], poly(D, L-lactid) [40,41], synthetic poly(3-hydroxybutyrate) PHB [42-44], poly(3-hydroxybutyrate) co poly(3-hydroxyvalerate) [45-48 (a-d)] and poly(caprolactone) [49-52] poly(3-hydroxypropionate) [53], poly(butylene succinate-co-butylene adipate) [54], poly(butylene succinate-co-caprolactone)[55]. PHB is miscible with polysaccharides such as cellulose and starch derivatives, PHB / cellulose acetate butyrate, cellulose acetate propionate [56-58]. PHB is immiscible with starch [59,60], poly(vinyl chloride), acrylonitrile-butadiene-styrene (ABS), poly(styrene), styrene acrylonitrile (SAN) [61-63], poly(ethylene) [64] and poly(propylene)[65].

1.6 The challenge to improve the processing and mechanical properties of PHB.

Main reasons for the brittleness of PHB and its elimination

1. The secondary crystallization that occurs during storage at room temperature, forms new lamellae in the amorphous phase.
2. It has a low nucleation density; therefore it forms large spherulites with cracks and splits, which have a negative influence on the mechanical properties.
3. It has glass transition temperature near ambient temperature.
To be more important in the future, the costs of biodegradable polymers are should of the order of conventional polymers, e.g. 1 kg PE or PP costs $1 but PHB cost approximately $2-8. They must meet the quality and processing conditions, as do PE and PP.

1.7 Main directions of improvements

For the development of a biodegradable material, based on PHB with better mechanical properties and long-term stability like, for instance, synthetic polymers it is necessary:

1. To prevent the degradation of chains in processing, which can be reduced by addition of lubricants and plasticizers.
2. To stop the secondary crystallization that occurs in the amorphous phase after aging time at room temperature, i.e., by suppression of the crystallization and shift of the glass temperature to lower values.
3. To investigate the effect of high temperatures melt processing, the cooling rate and holding time on the crystallization rate, crystal size, and number of spherulites.
4. To investigate the influence of the concentration of plasticizers on glass temperatures and other relaxation mechanisms.
5. To investigate the influence of additives on biodegradation behavior of PHB (soil burial, river water, compost conditions and the aerobic test).
6. To optimize processing technology like, for instance, injection molding and extrusion.

1.8 Blend development

Under the term polymer blends, the physical characteristics for two compatible or incompatible polymer components will be explained. It is the aim is to develop of 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 with 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 posses badly processable.
1.8 Blend development

It sticks on metal surface, and thermal unstably. For the physical point of view, the reasons the brittleness of PHB is 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.

1.9 Materials and blend preparation

PHB was supplied by COPERSUCAR from Brazil. It was synthesized by the fermentation of sugar, saccharose or syrups using *Alcaligens euthrophus*. It is a yellowish white powder and has a molar mass $M_w$ of 220 kg/mol, a melting point of about 173°C and a crystallinity of 55 %.

Another PHB was supplied by BIOMER (Dr. Haenggi); Krailling, Germany. It was synthesized by the fermentation of sugar by *Alcaligens euthrophus*. This polymer is a white powder with a molar mass $M_W$ of 230 kg/mol. It has a melting point of about 175°C and a crystallinity of 60 %. We have examined the two types of PHB from Brazilian and Germany in NMR and FT-IR. The spectra are identical and have the same peaks in NMR and FT-IR. The only difference is the colour.

PHB as a powder was blended with additives by mixing in a Brabender (kneader) at 170°C – 180°C and 50 rpm for 5 min or in a single screw extruder at a temperature of between 145°C (zone 1), 160°C (zone 2) and 170°C (zone 3) with 4 mm die and screw speed of 20 rpm. The strand (thread) was cooled in water and cut using a pelletizer. All additives are biodegradable substances. The mixed material (granulates) was compression moulded in a hydraulically heated press from 170°C – 180°C between two sheets of Teflon for 3 min without pressure and 2 min with pressure (50 bar). After molding, the sample is cooled between cold metal plates with water. Plasticizers like glycerol, tributyryrin, triacetin, acetyltriethylcitrat, acetyltributylcitrat and nucleation agents like, for instance, phthalimide, saccharin were used. Lubricants like glycerolmonostearate, glyceroltristearate, 12-hydroxystearat, and 12-hydroxystearicacid can also be used. The weight ratios of PHB / additives are listed in table 1.

1.10 Extruder

The blends are mixed in an Extruder. The first step is to produce the pellet form; the second step is to use the pellet to produce films, sheet, bottles and injection-molded parts. The task of the extruder or injection molding machine is to take the solid plastic and using heat, pressure and shear, to transform it into a uniform melt which can then be delivered to the next processing stage. The final melt must be uniform both in concentration and temperature. The
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pressure must be high enough to press the viscous polymer through an opening (die), which gives the desired shape to the extrudate.

A simplified Extruder diagram is shown in figure (1.3A). The size of the Extruder depends on the diameter of the barrel and the ratio of the length of the barrel to the diameter. A typical Extruder size for packaging applications has a barrel diameter between 4 cm to 20 cm, and a length to diameter (L/D) ratio of about 16:1. The Extruder contains three sections. The first section is maintained at a relatively low temperature. The second section is where the melting occurs and pressure is built up. Figure (1.3 b) is the schematic diagram of a single screw Extruder with chill roll and figure (1.3 c) is the injection-molding machine. The transition between the feed section and the compression section may be abrupt. Finally, the extruder outlet is the metering section. At the end of the barrel, the melted plastic leaves the Extruder through a die, which has been designed to give the desired shape to the stream of melted plastic. The polymer viscosity is dependent on both temperature and flow rate.

1.11 Cast film and sheet

For the production of cast film or sheet the Extruder is shaped like a slit die (rectangular profile) in the melt, the width of which is much greater than the thickness. The cast film and sheet are produced by extrusion of the melt to chilled chrome rolls. The plastic exits in a downward direction towards the chill roll. Contact is tangent (see figure 3B). The film travels in an S-pattern around at least two chill rolls. The first chill roll normally operates at a temperature of 40°C. An air knife is used between the plastic and chill roll; this leads to the formation of a film with better transparency and, thus increased stiffness and, thus, may also increase output. The film’s dimensions are controlled by the extrusion rate, melt temperature, cooling and take off speed.

1.12 Injection mould

Injection mould is used for producing base cups for bottles, margarine tubs, containers and packaging articles for the food industry. During injection, the plastic is melted in an injection-moulding machine like, for instance, an extruder used for producing cast film. It is equipped with a reciprocating screw that moves backwards and forwards in the barrel. When a sufficient volume of melt has accumulated, the screw stops rotating and is driven forward mechanically or hydraulically, thus, injecting the plastic through a nozzle into the mould through the spree, a system of runners and finally into the cavity via the gate (figure 3C).
Once the mould component is cool enough, it solidifies and the mould opens automatically. The cycle time depends on the size of the molded part and molding conditions. It is very important to balance the flow of plastic so that the mould cavities are filled evenly and to the same extent; this means that the distance and geometry of cavity from the spree should be equal.

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<th>Table 1: Preparation</th>
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Figure 1.3A: Plastic Extruder.

Figure 1.3B: Cast film using a chill roll.

Figure 1.3C: Injection mould.