DEPARTMENT OF INDUSTRIAL MANAGEMENT AND TECHNOLOGY

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Poly(butylene succinate): A Promising Biopolymer

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ABSTRACT

Since 1976, plastics play a major role in everyday life and they have been the most used material in the world. Plastics are often selected over traditional materials because of their superior properties and lower cost. Their versatility enables their use in applications ranging from clothing and packaging to high-tech composites. Currently manufacturers and researchers are targeting in new biobased products able to be used in several applications with packaging in first position. Owing to its biodegradability, wide processing window, and balanced mechanical properties, poly(butylene succinate) (PBS) and its copolymers have attracted much interest.

This paper deals with PBS, this fairly new but a lot promising biopolymer. PBS synthesized from succinic acid and 1,4-butanediol exhibits balanced performance in thermal and mechanical properties as well as thermoplastic processability compared with other common plastics. In this paper, synthesis, processability, properties, biodegradability and recycling of PBS and its copolymers will be outlined. In addition, industrial production and applications will be briefly summarized.

In *Chapter 1* PBS monomers are presented.The synthesis of succinic acid and butanediol, are briefly reviewed, focusing on biobased production methods. Moreover we present the manufactures of these building blocks worldwide.

In *Chapter 2* PBS preparation processes are described. Two-step transesterification polymerization, direct polymerization, condensation polymerization followed by chain extension, enzymatic polymerization and direct polyesterification under microwave irradiation are the ones we lay out about. Except of PBS homopolymer, we also introduce the copolymers' and branched PBS preparation processes. Industrial production is also reviewed.

In *Chapter 3*, characterization and critical properties of the biopolymer are presented, focusing on molecular weight determination, gel permeation chromatography, end group analysis, viscosity, melt flow index, thermal /mechanical properties and transition, melting and thermal degradation and crystallization.

In *Chapter 4*, processing and applications of PBS are briefly described. Several types of additives and processing methods such as extrusion, injection molding and thermoforming are defined. Moreover there is a review on all possible application fields of PBS.

In *Chapter 5*, we get through degradability and recycling of PBS. Non enzymatic and enzymatic hydrolytic degradation, environmental biodegradation and thermal degradation are presented. PBS possible recycling techniques reviewed are mechanical recycling, chemical recycling and incineration.

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CHAPTER 1: POLY (BUTYLENE SUCCINATE) BUILDING BLOCKS (PBS MONOMERS)

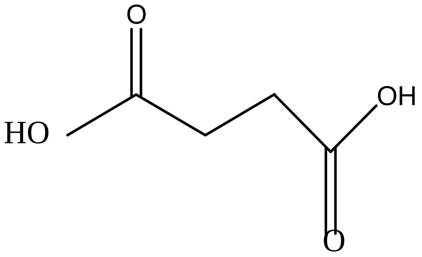
1.1. Succinic acid technology and properties

1.1.1. Introduction

In 2004, the U.S. Department of Energy (DOE) [1] released a report identifying 12 chemicals that could be produced from sugars, through microbial fermentation. These building blocks were of great interest because they could be converted into various high-value biobased chemicals and materials. The main criteria for the top 12 chemicals were the following:

1) multiple functionalities suitable for further conversion as derivatives or molecular families
2) production from both lignocellulosics and starch
3) a carbon number classification framework of one to six carbon compounds (C1-C6 monomers)
4) non aromatics derived from lignin
5) not already supercommodity chemicals
6) strategic fit for lignocellulosic and starch biomass within the biorefinery
7) value of the building block and its derivatives as a replacement or novel chemical
8) the technical complexity of each part of the pathway transformation (sugars to building blocks and building blocks to derivatives)
9) the building block's potential to produce families or groups of similar derivatives

At the top of the list was succinic acid. Succinic acid is an important platform molecule derived from petrochemical or biobased feedstocks and can be transformed into a wide range of chemicals and polymers. Petroleum or coal based succinic acid is cheaper than biobased but with future development it will become competitive. Concerning succinic acid, its molecular formula and its actual and potential pathways from sugar are shown in scheme 1.1 and Table 1.1 respectively.



Scheme 1.1. Molecular formula for succinic acid

Table 1.1. Identification of the actual and potential pathways from sugar [1]

Building block	Yeast of fungal	Bacterial	Yeast of fungal	Bacterial	Chemical and catalytic processes	Biotransformation
Succinic acid	Aerobic fermentation		Anaerobic fermentation		CHEM-enzyme transformations	
	x	x		x		x

1.1.2. Properties of succinic acid and its applications

Succinic acid or butanedioic acid belongs to dicarboxylic acids. Their general formula is $HOOC(CH_2)nCOOH$, where n=0 for oxalic acid, n=1 for malonic acid, n=2 for succinic acid, n=3 for glutaric acid etc. The range of carbon chain length is from 2, and longer than C 24 is very rare. Carboxylic acids have industrial application directly or indirectly through their derivatives, such as acid halides, esters, salts, and anhydride forms. Dicarboxylic acids are useful in a variety of industrial applications including:

- Plasticizers for polymers
- Biodegradable solvents and lubricants
- Engineering plastics
- Epoxy curing agent
- Adhesive and powder coating
- Corrosion inhibitor
- Perfumery and pharmaceutical
- Electrolyte

There are almost innumerable esters obtained from carboxylic acids. Esters are formed through condensation reaction between an acid and an alcohol. Lower chain esters are used as flavoring base materials, plasticizers, solvent carriers and coupling agents. Higher chain compounds are used as components in metalworking fluids, surfactants, lubricants, detergents, oiling agents, emulsifiers, wetting agents textile treatments and emollients. They are also used as intermediates for the manufacture of a variety of target compounds. Esters provide a wide range of viscosity, specific gravity, vapor pressure, boiling point, and other physical and chemical properties for the proper application selections.

Focusing on succinic acid, it occurs naturally in plant and animal tissues. It plays a significant role in intermediary metabolism (Krebs cycle) in the body. Krebs cycle (also called citric acid cycle, tricarboxylic acid cycle) is a sequence process of enzymatic reaction, in which a two-carbon acetyl unit is oxidized to carbon dioxide and water to provide energy in the form of high-energy phosphate bonds.

Succinic acid is a colorless crystalline solid, soluble in water, slightly dissolved in ethanol, ether, acetone and glycerin, not dissolved in benzene, carbon sulfide, carbon tetrachloride and oil ether. The properties of succinic acid are listed in the table 1.2. [2, 3].

Table 1.2. Physical properties of succinic acid [3]

CAS Number	110-15-6
Appearance	White Crystalline Product
Molecular Formula	$(CH_2COOH)_2$
Physical State	Odorless white crystals
Molecular Weight	118.09 g/mole
Melting Point	188°C
Boiling Point Decomposes	at 235°C
Specific Gravity	1.56 $25^{o}C/4C$
Assay (dry basis)	99.5% w/w
Solubility	100g/100ml at 100°C in water 7.69g/100 ml at 25°C
Residue on Ignition	0.025% w/w
Lead Content	2 mg/kg
Arsenic Content	3 mg/kg
Moisture Content	0.5% w/w
pKA1	4.21
pKA2	5.64

Traditionally, succinic acid is used in four application regions [4]. The largest one is as a surfactant, extender and foaming agent. The second region is as an ion chelator, where it is used in order to prevent the corrosion and spot corrosion of metal in the electroplating industry. The third is as an acidulant, a pH regulator and flavoring agent in the food and drink industry and the fourth is the production of pharmaceutical products, including antibiotics, amino acids, and vitamins. The total market size for these four existing uses of succinic acid is more than $ 400.000.000 per year concerning a current worldwide use of about 20.000–30.000 tons/year, with an increasing rate of 10% a year [5].

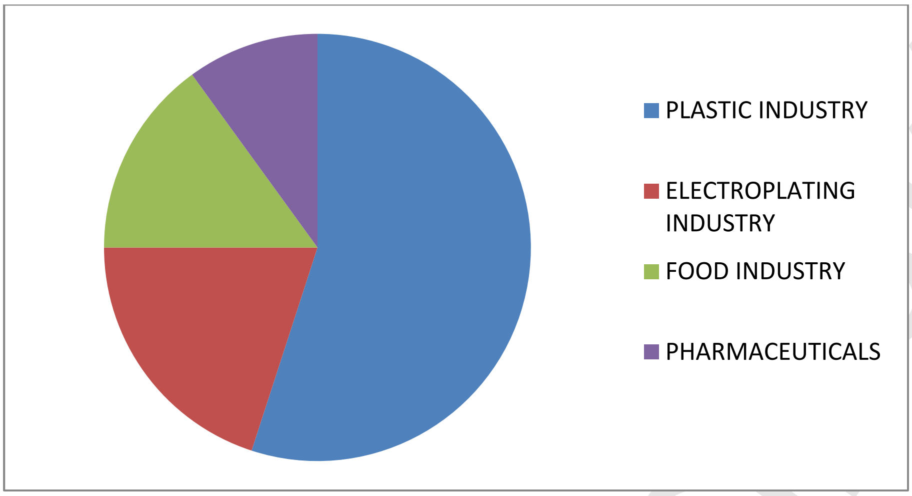


Figure 1.1. Succinic acid market shares [4]

In addition, succinic acid is an important chemical building block and the world market of its derivatives has a potential that is estimated to be 270.000 tons/year [5,6]. Taking into account the current improvements in the microbiological succinic acid production, which will lead to a competitive price, the production routes from succinic acid will become economically more viable and more important.

A major group of possible succinic acid derivatives consists of: butanediol, tetrahydrofuran, gamma-butyrolactone, adipic acid, N-methyl pyrrolidinone, 2-pyrrolidinone, succinic acid esters and succinate salts (figure 1.2) [7]. Butanediol and succinic acid polyesters (such as poly (butylene succinate), PBS) are going to be presented later in more detail.

<u>Butanediol:</u> is a raw material used for the synthesis of films, fibers, engineering plastics and adhesives. Biological routes are the most widespread used. There is a great interest in biobased butanediol concerning the reduction of the use of petroleum-based feedstocks in light of global oil prices.

<u>Tetrahydrofuran (THF):</u> is a solvent and key ingredient of adhesives, printing inks, and magnetic tapes. It is also suggested as a feedstock for an alternative of the adipic acid production via carbonylation, but this route is not that competitive with the current one [8]. On the other hand, THF is a precursor for the production of poly (tetramethylene ether glycol) (PTMEG), used in the production of polyurethane polymer [9, 4].

<u>Gamma butyrolactone (GBL):</u> is used as a solvent for polymers and alcohols, as a chemical intermediate, a raw material for pharmaceuticals, and as a component of herbicides, pharmaceuticals and rubber additives [10, 11]. The GBL can also be converted to 2-pyrrolidone. More than 230.000 tons of GBL are produced per year worldwide.

Adipic acid: is a raw-material chemical used in the manufacture of lubricants, foams and food products. Benzene is the main feedstock for adipic acid production but there are also two alternative methods involving succinate [4, 8, 12]. Adipic acid is also the precursor to nylon 6,6.

Pyrrolidinones: are materials that can be derived from GBL, and address a large solvent market. Succinic acid through the fermentative production of diammonium succinate can be directly converted to pyrrolidinones.

Succinate salts: could replace current salts by offering improved performance characteristics and more neutral effects on surfaces and the environment .Succinic salts may also be used as additives to animal feed.

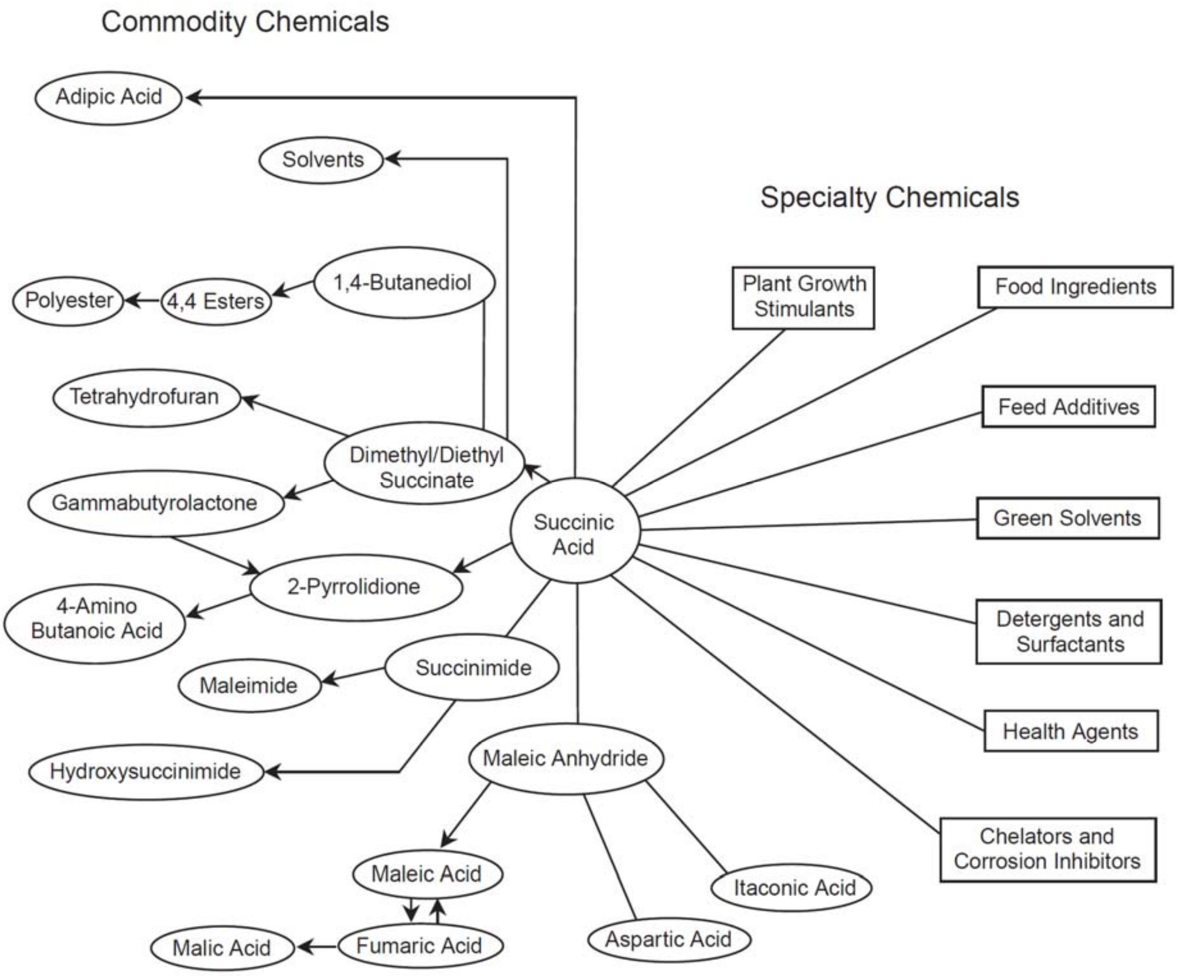
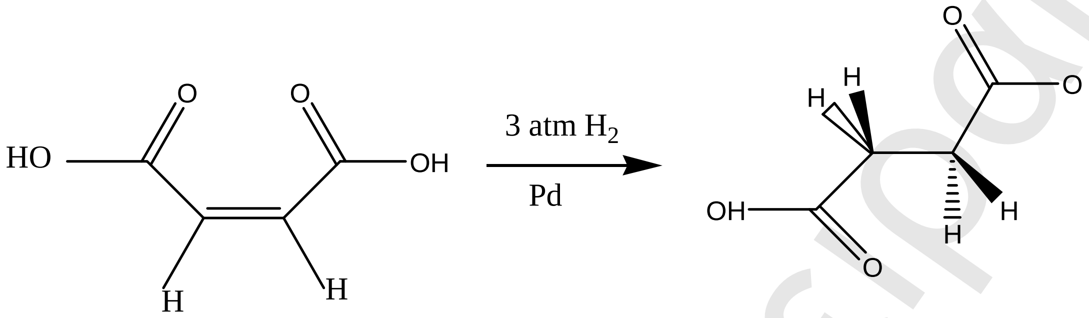


Figure 1.2. Succinic acid derivatives [4]

1.1.3. Succinic acid production methods

The common method of synthesis of petrochemical succinic acid is the catalytic hydrogenation of maleic acid or its anhydride (scheme 1.2).



Scheme1.2. Hydrogenation of maleic acid to succinic acid

The lack of renewability and the rising price of the fossil resources have limited the use of petrochemical succinic acid for a wide range of applications. Consequently, the interest for fermentation methods arises rapidly. Bio-succinic acid is produced by fermentation of starch or oligosaccharides (C-5, C-6 sugars) containing renewable resources. This fermentation of carbohydrates may also yield other valuable chemicals, such as lactic acid, acetic acid, formic acid, and alcohols. The yield of all these chemicals may vary according to the micro-organism and cultivation technology used. The forlumas of the fermentation reactios are presented in schemes 1.3 and 1.4.

$$\text{glucose} + CO_2 + KOH \longrightarrow K_2SA\ \text{(succinic salt)} + ATP\ \text{(energy)}$$

$$K_2SA\ \text{(succinic salt)} + H_2SO_4\ \text{(sufuric acid)} \longrightarrow K_2SO_4\ \text{(salt)} + H_2SA\ \text{(succinic acid)}$$

Scheme 1.3. Bacteria based production of succinic acid

$$\text{glucose} + CO_2 \longrightarrow H_2SA\ \text{(succinic acid)} + ATP\ \text{(energy)}$$

Scheme 1.4. Yeast based production of succinic acid

Although there are a few industries producing biobased succinic acid in commercial scale, it is important to mention that a minimum productivity of 2,5 g/l/h needs to be achieved in order for the process to be economically competitive. In addition, it is essential for commercial fermentations to operate using minimal nutrients. Expensive nutrient components, such as yeast extract and biotin, must be eliminated. The nutrient requirements should be limited to the use of corn steep liquor or equivalent. In an ideal situation, the fermentation is carried out at low pH, most preferably without requiring any neutralization. The cost of neutralization is not necessarily cost prohibitive, but the conversion of the salt to the free acid does add significant cost [1].

When succinic acid is synthesized from petrochemical sources, it is labeled as chemically produced, whereas succinic acid from bioproduction is considered naturally produced as it is sourced from biomass [4]. This distinction of chemical versus natural production can change the areas in which succinic acid can be used as well as affect the selling price. Industries, such as foods and pharmaceuticals will prefer to use succinic acid produced from renewable resources to avoid potential health hazards from production residues, even though the product is identical through both production methods [13].

Petrochemical Production of succinic acid

Succinic acid is most commonly produced by hydrogenation of maleic anhydride or maleic acid or recovered from a byproduct stream in the production of adipic acid. Some industrial petrochemical routes applied for succinic acid production are:

- Separation of succinic from a mixture of different carboxylic acids after paraffins' oxidation.The following reactions occur in the reactive extraction of carboxylic acids with tertiary amine extractants (scheme 1.5).

$$\text{(I)}\ \ HA \rightleftharpoons H^{+} + A^{-}$$

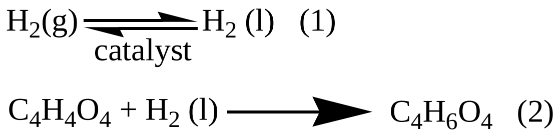
$$\text{(II)}\ \ R_3N + H^{+} \rightleftharpoons R_3NH^{+}$$

$$\text{(III)}\ \ R_3NH^{+} + A^{-} \rightleftharpoons R_3NHA$$

$$\text{(IV)}\ \ R_3N + HA \rightleftharpoons R_3NHA$$

Scheme 1.5. Reactive extraction for succinic acid

- Catalytic hydrogenation of maleic acid or trans-maleic acid. The reaction from maleic anhydride to succinic acid begins by hydrolysis, breaking one of the single bonds between carbon and oxygen, forming maleic acid. The addition of hydrogen breaks the carbon-carbon double bond and completes the reaction, forming succinic acid as it is shown in scheme 1.6:

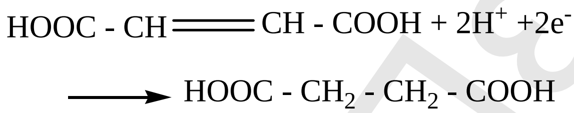


$$H_2(g) \underset{catalyst}{\rightleftharpoons} H_2\,(l) \quad (1)$$

$$C_4H_4O_4 + H_2\,(l) \longrightarrow C_4H_6O_4 \quad (2)$$

Scheme 1.6. Succinic acid from maleic anhydride

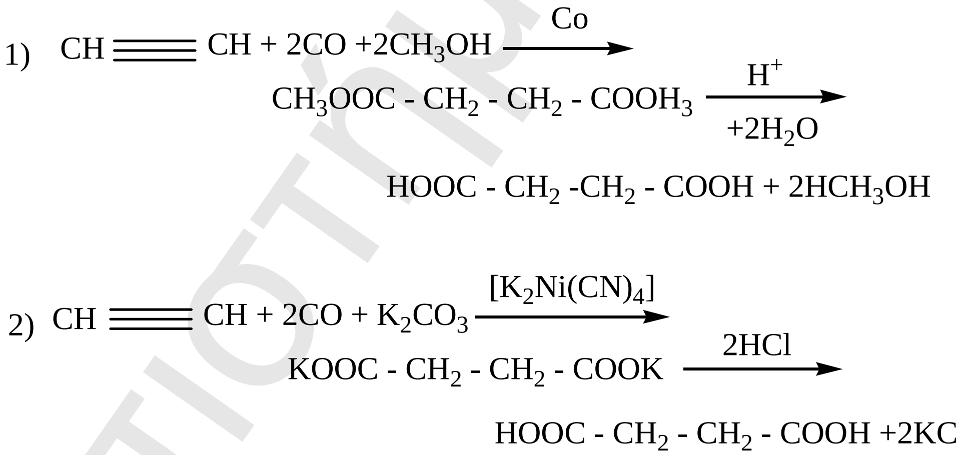
- Electrochemical synthesis from maleic anhydride in a bipolar membrane or nonmembrane cell. The electroreduction of maleic acid is a two electron, irreversible, diffusion-limited process as shown in scheme 1.7:



$$HOOC-CH{=}CH-COOH + 2H^+ + 2e^- \longrightarrow HOOC-CH_2-CH_2-COOH$$

Scheme1.7. Succinic acid through electroreduction of maleic acid

- Production from acetylene, carbon monoxide, and water catalyzed by $[CO(CO)_4]$ in an acid medium under a pressure of 2,94–49,03 MPa at 80–250°C.The methods known for the preparation of succinic acid comprise at least two stages according to the equations in scheme 1.8 :



$$1)\; CH{\equiv}CH + 2CO + 2CH_3OH \xrightarrow{Co} CH_3OOC-CH_2-CH_2-COOH_3 \xrightarrow[+2H_2O]{H^+} HOOC-CH_2-CH_2-COOH + 2HCH_3OH$$

$$2)\; CH{\equiv}CH + 2CO + K_2CO_3 \xrightarrow{[K_2Ni(CN)_4]} KOOC-CH_2-CH_2-COOK \xrightarrow{2HCl} HOOC-CH_2-CH_2-COOH + 2KC$$

Scheme 1.8. Succinic acid production from acetylene, carbon monoxide and water

Among them, electrochemical synthesis from maleic anhydride is a generally applied process for succinic acid, which has the advantage of high yield, low cost, high purity of the final product, and very low or no waste formation. Succinic acid produced by the electrochemical process can be used in food and pharmaceuticals [14]. The used maleic anhydride is produced from n-butane or benzene [15, 13].

Various heterogeneous catalysts have been studied concerning the aqueous phase hydrogenation of maleic acid to succinic acid. Pd/Al_2O_3 catalyst, in a trickle bed type reactor. Effects of

Pt or Pd on various supports in the aqueous phase of hydrogenation have also been investigated. It has been reported to reach a 99,5% yield when a mixture of maleic acid, water and Pd/C catalyst is autoclaved at 100 ^{0}C with hydrogen bubbling .The hydrogenation of maleic acid in aqueous cobalt chloride and potassium chloride solutions has been reported to give 41% succinic acid in the presence of a Zn/Hg catalyst and 22% in its absence. Succinic acid has also been prepared chemically by treating maleic acid with 50% H_3PO_2 at room temperature in aqueous NaOH/ EtOH with an average yield of 83% . Ru is also known to be a good catalyst for hydrogenation in the presence of water. Further, it is cheaper than Pd and Pt and it is equally effective for hydrogenation of fumaric acid to succinic acid. Succinic acid may also be obtained at high yields by the hydration of succinic anhydride in an autoclave at 200 ^{0}C.

Although the yields in some of the above processes are good, their practicability is limited by several factors such as: the requirement of adding a supporting electrolyte in the electrochemical cell, the saturation of the medium with succinic acid before electrolysis, the need for costly catalysts or reagents, and the separation of supporting electrolyte, catalyst and/or unreacted reagents from the reaction mixture/product.

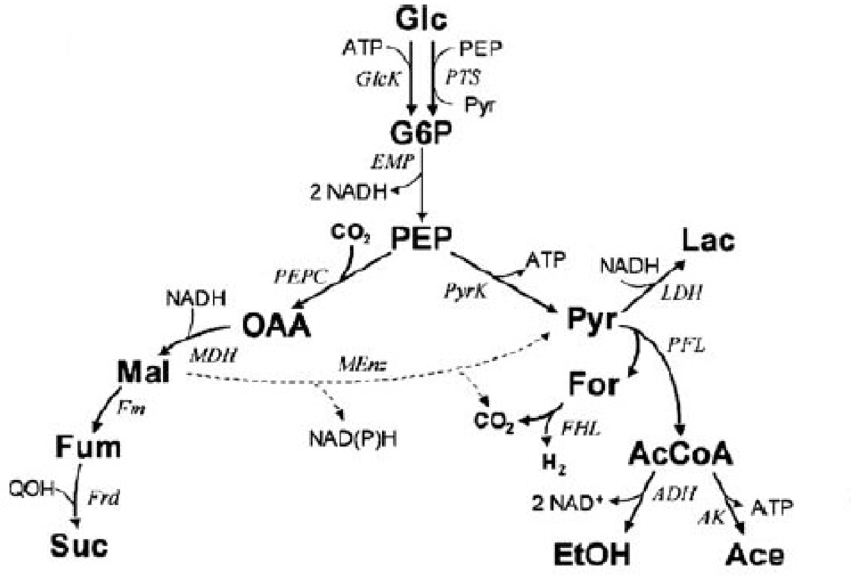
Except hydrogenation, succinic acid can be synthesized in excellent yields by the galvanostatic reduction of maleic acid at stainless steel, Cu and Pb cathodes in an ion exchange membrane flow cell. This method demonstrates the advantages of using a highly conductive solid ion exchange membrane film between the two electrodes in a flow cell, which employs a catholyte without supporting electrolyte for the electroreduction of maleic acid. Hence, the requirement of additional separation steps, otherwise required in conventional methods, is made redundant. Cyclic voltammetric studies indicate a two-electron diffusion limited irreversible reduction of maleic acid to succinic acid [16].

Industries producing petrochemical succinic acid all over the world are following patented routes regarding catalysts, water reduction and high yield at a low cost by supplying an aqueous solution of maleic acid. In this case the solution has a concentration of 10-60 wt %, preferably 20-40wt % and the hydrogen pressure is set at about 5-50kg/cm at 60-150 ^{0}C .

Bio-based Production of succinic acid

Succinic acid can be produced through fermentation by bacteria isolated from ruminant animals, converting glucose to succinic acid, along a portion of the reductive cycle of tricarboxylic acid (TCA) cycle [17]. Fermentation production has attracted interest the last decades regarding increased knowledge and metabolic technology. To have an economically viable biosuccinic acid process, it should be competitive with the current applied chemical process. Based on the petrochemical analogue (maleic anhydride), the U.S. Department of Energy have set the targeted production price of biosuccinic acid at 0,45 dollars/kg. The most important parameters determining the viability of a method are: 1) yield 2) (purity) and 3) production rate. Only yield is related to the cost of raw feedstock. Wilke [18, 6] calculated that a yield of 100 %, a rate of 3 g/l/h and purity up to 250 g/l would result in a total production cost of 0,45 dollars/kg.

First reaction step in a typical fermentation process is glucose conversion to glucose-6-phosphate by hexokinase .Next follows the production of phospho-enol-puryvate (PEP), from which the metabolic route can take one of two paths depending on the amount of CO_2 available in the system. With amble supply of CO_2, the microorganism favors succinic acid production. On the contrary, if there is not enough CO_2 the metabolic pathway leads to different end products, such as formate, ethanol and acetate [7]. Next reaction is hydrogenation in order to produce malate, which is converted to fumarate by fumarase with water removal. In this way, succinate in ionic state is formed, which is common as the pH range of production is above pKa values for succinic acid [4]. Succinic acid as an end product can be created by protonating the succinate ion. A theoretical yield of succinic acid production has been estimated to 1,17 moles per mole of glucose based on stoichiometry by McKinlay [7]. All the reaction steps are shown in scheme 1.10.



Scheme 1.9. Simplified metabolic map of E. Coli fermentation for succinic acid production [7]

Fermentation is a production method that has by-products. Acetic acid, formic acid are some of them and they are observed in concentrations 9,2 g/l and 6,1 g/l respectively. Although the values are really small comparing to succinic acid production of 27,2 g/l, the separation is the most expensive and time consuming step of the whole process [19]. Concerning the downstream purification cost, this normally accounts more than 60 % of the total production cost and it is crucial to develop a more economical process purification process for succinic acid.

Several methods for the succinic acid recovery and purification have been developed including reactive extraction, ion exchange resins, electrodialysis, precipitation and nanofiltration [20]. Glassner and Datta [21] suggested a conventional electrodialysis system to remove succinic acid from the fermentation broth after ultrafiltration. In this method, ionized compounds are separated from non-ionized compounds by ion exchange. Hong and Hong [22] have stated that electrodialysis could be used in conjunction with other separation methods, notably amine-based extraction [20]. Electrodialysis is a method that has significant potential, but there are also some shortcomings with using this system on an industrial scale. One of the most glaring problems is that electrodialysis requires energy to function. Given that energy costs are on the rise and electricity may come from non-renewable resources, it would seem counterintuitive to use this method, since the intent of succinic acid production via fermentation is to reduce the use of fossil fuels and provide a more environmentally friendly process [23]. A succinic acid purity of 80% can be achieved.

Precipitating succinic acid out of solution is a separation process that was first proposed by Datta [24]. In this process, after the fermentation reaches completion, solids are centrifuged and separated out of the fermentation broth by addition of calcium dihydroxide, which simultaneously neutralizes the fermentation broth. Succinic acid is recovered by filtration and further purified by acid and ion exchangers. Precipitation appears to be the most common and simplest method for succinic acid separation, but it is also one of the most inefficient processes from an environmental and economic standpoint. With this downstream process, a purity of 95% can be achieved.

The extraction of succinic acid with an amine-based extraction method has been investigated by Huh[26]. It is a promising method of separation because separation is possible in-situ at room temperature and pressure, so no pre-treatment is required for this method to function properly [26]. This process is based on reversible reaction between extractant and extracted carboxylic acid. There are additional steps that must take place to continue the process of separating and purifying succinic acid, such as vacuum distillation and crystallization, but given that the byproduct organic acids have been removed, this step becomes easier, reaching a final purity of 99,8% with a yield of 73,1% [20,23].

Nanofiltration is a relatively new method for separating out the different byproducts of the fermentation broth from succinate. Kang and Chang [27] studied how two different nanofiltration membranes separated the main products of glucose fermentation by *A. succinogenes*, including succinate, formate, and acetate. The results indicated that the filters had a very high retention of succinate, the only divalent ion product [20]. While nanofiltration shows promise there are still some aspects of the process that are not addressed, such as the price of membranes, membrane fouling and the application of this separation method in real fermentor broth.

1.1.4. Fermentation feedstock and microorganisms in bio-based production of succinic acid

Among many fermentation feedstock studied, cane molasses, whey, glycerol, lignocellulosic hydrolyzates and cereals have proven to be adequate for fermentation processes. Cane molasses is a by-product of sugar industry consisting of water, carbohydrates, heavy metals, colloids, vitamins and nitrogenous compounds [15]. Whey is a side stream from milk industry and it is already used in several fermentation processes with great success. Succinate production is one of them as well. Glycerol is increasing considerably due to biodiesel production. It is meant to be a very suitable carbon source for succinic acid production by *A. succiniproducens*, with high yields and less by-products.

Lignocellulosic material can also serve as a carbon source and replace glucose. Untreated hydrolysates can be used but with approximately half of the productivity of the alkaline treated material. At last, a novel biorefining concept has been introduced regarding the biosynthesis of succinic acid from wheat flour.

Various microorganisms and strains have been reported to produce succinic acid. However the choice of the production host is very diverse. *A.succinogenes* and *A. succinoproducens* were the first identified natural succinic overproducers.

A.succinogenes is a facultative anaerobic, capnophilic, mesophilic, pleomorphic, Gram-negative rod and member of the *Pasteurellaceae* family isolated from bovine ruminal. This strain shows a distinctive ability to produce a relatively large amount of succinic acid from a broad range of carbon sources such as arabinose, cellobiose, fructose, galactose, glucose, lactose, maltose, mannitol, mannose, sorbitol, sucrose, xylose or salicin under anaerobic condition [28]. Guettler et al. [29] investigated also 130Z strain which was able to produce larger amounts of succinic acid and were more resistant to it. *A.succinogenes* variants can produce succinate up to 110 g /l at a yield of 83–87 % if the pH is maintained with magnesium [28, 30]. Strain 130Z produced 66,4 g/l succinic acid by consuming 98,3 g/l of glycol after 84 h of fermentation. Compared to the other major producers of succinic acid, there are several advantages of this bacterium including tolerance to high levels of substrate, high resistance to product inhibition, and high production rate. It also has a high tolerance of oxygen, low production of unwanted acid by-products and can use a number of substrates in comparison to other succinic acid producing bacteria. Many sources state that *Actinobacillus succinogenes* is the microorganism of choice for creating an industrial process, having a high tolerance of succinic acid [31].

A. succinoproducens is a strictly anaerobic, capnophilic, mesophilic, pleomorphic, gramnegative spiral rod and an opportunistic pathogen, isolated from the throat and feces of a beagle dog [32]. The broad spectrum of carbon sources it ferments has allowed succinate production of several complex sugar mixtures originating from for instance wood hydrolysates and whey. Lee et al. [20] reported the use of glycerol as carbon source which leads to an increased succinic yield (1,33 mole/mole). As typical a capnophilic A. *succiniciproducens*, requires high carbon dioxide for efficient growth. Addition of hydrogen gas to the sparging gas can also increase yields and production rates and that because of the increase in NADH in the cell. Lee et al. reported also a maximum succinic acid yield of 0,91 mole/mole and a maximum productivity of 1,8 g/l/h.

M. succiniciproducens is a facultative anaerobic, capnophilic, mesophilic, gram-negative rod and similar to *A. succinogenes*, and a member of the *Pasteurellaceae* family. *M. succiniciproducens* ferments a wide variety of substrates and hydrolysates [17]. A disadvantage of this strain is the auxotrophies exhibitions. In contrast to *A. succinogenes*, *M. succiniciproducens* has a complete TCA cycle and can efficiently grow in aerobic as well as in anaerobic conditions. It produces succinic acid as a major product, acetic and formic acids as the second major ones from various carbon sources under 100% CO_2 condition at pH of 6,0–7,5. *M. succiniciproducens* leads to a succinic acid productivity of 3,9 g/l/h [17]. Moreover, the efficient and economical production of succinic acid was possible by using a whey-based medium containing corn steep liquor instead of yeast extract. In batch cultures, the final succinic acid concentration of 11,73 g /l was obtained from the pre-treated wood hydrolysate based medium, resulting in a succinic acid yield of 56% and a succinic acid productivity of 1,17 g/ l/ h while the corresponding continuous cultures gave the succinic acid yield and productivity of 55% and 3,19 g/ l/ h, respectively [33].

E. coli under anaerobic conditions produces a mixture of organic acids. In order to increase the yield of succinic acid in relative to other acids, different *E. coli* mutants have been developed. Two such mutants are AFP184 and AFP111. The recombinant *Escherichia coli AFP184* strain showed a production rate and yield substantially higher those of natural producers. Productivity up to 3 g/ l/h was obtained by dual-phase fermentations of sugar in high concentrations. *E.coli AFP184* is a strain easy to handle produce succinic from glucose, fructose, xylose and mixtures of glucose and fructose and xylose with productivity in the range of 1,5 – 2,9 g/l/h [34].

E. coli AFP111 is being used to ferment sugars derived from wood wastes and plant crop residues. This novel E. coli strain has been patented for the production of succinic acid from corn-derived glucose, and it is being genetically engineered to improve the conversion rates of different types of sugars very efficiently [1]. In 2002 succinic acid production was examined in *E.coli AFP111* using dual-phase fermentations, which comprise an initial aerobic growth phase followed by an anaerobic production phase. Using the best transition time, fermentations achieved a final succinic acid concentration of 99,2 g/l with an overall yield of 110% and productivity of 1,3 g/l/ h.

Enterococcus faecalis RKY1 was also reported to produce succinic acid with a high productivity of up to 17,1 g/ l/ h starting from 80 g/ l fumarate and glycerol in a continuous fermentation process

[35,36,37]. The yield of bioconversion was enhanced about 1,2 times by addition of glucose and the amount of succinate produced in the high cell culture is about three times higher than was the case in the low cell culture. The maximum concentration of 65,9 g/l succinate was obtained at pH 7.0. These results indicate that *Enterococcus sp. RKY1* strain can produce succinate from fumarate at a significantly higher yield and higher rate than any amplified E. coli. Since glycerol, a renewable resource, derived from the manufacture of biodiesel fuel can be used as starting material, the advantages of using glycerol as a substrate include that succinate can be produced with a cheaper raw material in high concentration with high purity and high yield, permitting economic recovery of succinic acid.

In 2011 Raja [38] isolated a novel succinic acid producing bacterium from cow bovine rumen and studied succinic acid production using different synthetic carbon sources such as glucose, sucrose, fructose, dextrose, starch and cellulose and different crude carbon sources such as rice straw, sorghum stalk, baggase and sugar mill waste (figure 1.3.). The fermentation process was carried out under CO_2 atmosphere with N_2 gas. The effect of pH, temperature and initial dextrose concentration were studied and optimized. The optimum fermentation conditions for the newly isolated strain were found to be: pH – 6,5, temperature 30°C and initial dextrose concentration 10 g/L. At these optimized condition, the maximum production of succinic acid was found to be 15g/l.

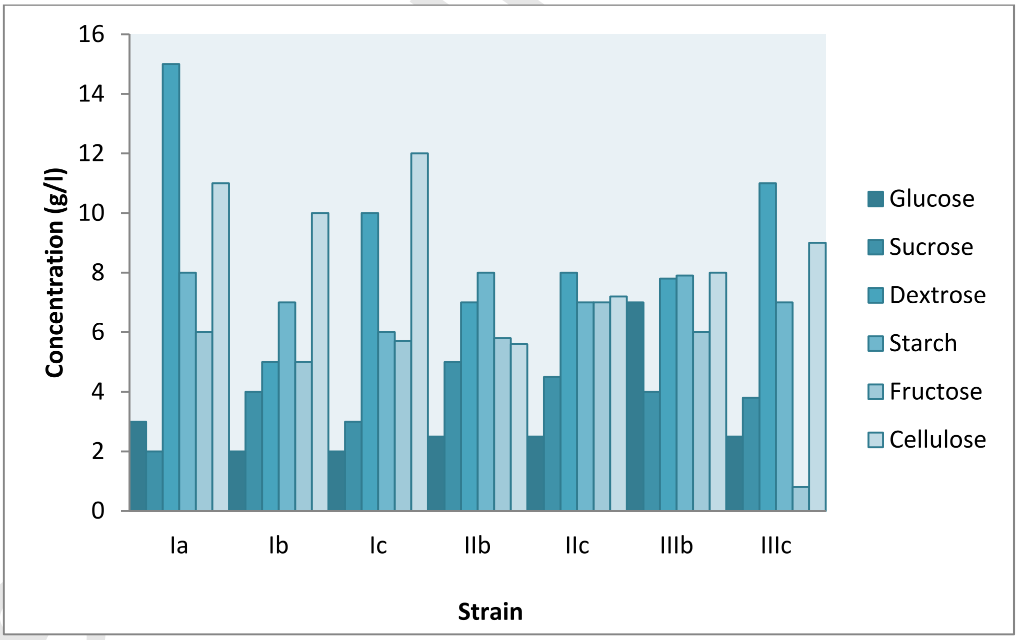


Figure 1.3. Production of succinic acid from different isolates (Ia, Ib,Ic,IIb,IIc,IIIb and IIIc are different types of strains) using various synthetic carbon sources [38]

For an economical biobased succinic production, several improvements should be made, including limiting the use of low cost amino acids, high yield and inexpensive carbon sources. The optimization of a biosuccinate production process is been the topic of many research in the past two decades. Although some of the process performances are very promising, many problems have been uncovered over the years. Production rate and by-product formation should be the points of attention. Novel ways to increase the production rate should be developed and potential by-product formation pathways should be investigated. In conclusion performances of succinic acid production by various microorganisms are gathered in table 1.4.

Table 1.4. Succinic acid production by various microorganisms

Microorganisms	Fermentation strategy	Feedstock	Time (h)	Succinic acid concentration (g/l)	Yield (g/g)	Productivity (g/l/h)
A.Succinogenes	Repeat- batch	Glucose	38,5	33,9	0,86	0,88
130Z	Batch	Glucose	84	66,4	0,67	0,79
M. succiniproducens	Batch	Glucose	7,5	14	0,70	1,87
	Batch	Whey	11	13,5	0,72	1,22
A. succiniproducens	Continuous	Whey	0,085 /h	24	0,72	2,10
	Fed- batch	Glucose and glycerol	22	29,6	0,97	1,35
	Batch	Glucose	30	33	0,93	1,10
Recombinant E. coli						
AFP111	Dual phase fed- batch	Glucose	76	99,2	1,10	1,30
AFP184	Dual phase fed- batch	Glucose	24	45,4	0,92	2,84
		Fructose	-	27,7	0,46	1,54
		Xylose	-	29,2	0,69	1,79
		Glucose and Fructose	-	52	0,73	2,89
		Glucose and Xylose	-	31,2	0,57	1,73

1.1.5. Advantages and disadvantages of biobased succinic acid production

Compared to the chemical process, the fermentation process has both advantages and disadvantages. One of the obvious advantages is the mild conditions that require less energy input. Moreover, fermentation is characterized by the independence of the fossil feedstock and the fixation of CO_2. Theoretically, succinate fermentations consume 1 mole of CO_2 per mole of succinate produced, while 1 mole of glucose and 2 mole of CO_2 are transformed into 2 mole of succinate. The manufacturing process produces also less toxic waste resulting in the same chemical as in petrochemical production.

On the other hand, fermentation procedures require large occupation space of the factory and much longer fermentation time. They also imply large amounts of aqueous solutions of salts which pose an ecological problem. In addition, the complicated separation and purification steps of the final product lead to a high production cost. Fermentation reaction has also problems, because cells are living organisms and as production takes place, product inhibition can occur and cell growth and synthesis stop because more energy is required to maintain cells [17]. Moreover, by-products of the fermentation (acetate, formate, etc.) lead to a distortion of the balance. They can limit succinic acid production as well as take away from the carbon source used by the bacteria to make the main product, reducing the yield of the desired product [25]. The idea of altering organisms in a way to reduce or eliminate by-products has been suggested and some work has been done to alter the genetic code of bacteria to ensure that only specific genes are expressed, limiting the number of undesirable products [20].

Until recently, the main problem of fermentatively produced succinic acid was the price. The cost is mostly increased by the required nutrients and the by-product recovery. The price of nutrients is higher than the price of carbohydrate nutrients, so it has to be part of economic consideration. Efforts have been made to lower the price by making the production process more efficient. On the other hand, maleic acid price rose seriously in the past couple of years. The main difference between the two is therefore slowly diminishing, creating opportunities for succinic acid as substitute of maleic acid, especially since industrial demand of the later is still increasing. A general comparison between fermentation and petrochemical production is shown in the table 1.5.

Table 1.5. Comparison between chemical and fermentative routes

	Petrochemical production	Fermentation
Origin	Nonrenewable feedstock (petrochemicals)	Biobased feedstock (carbohydrates)
Price	Cheaper than renewable sources	Downstream processes high cost
Routes	▪ Developed routes ▪ Established technology	▪ Routes under constant improvement ▪ New technologies
Yield	High	▪ Side products ▪ Diluted media ▪ Long reaction time
Disadvantages	▪ Availability expected to decrease in time ▪ High energy demands ▪ Catalysts disposal issues	▪ Sensitivity of microorganisms ▪ Nutrient requirements ▪ Complicated product recovery ▪ Wastes
Public awareness	Decreasing popularity	Increased interest

1.2. Manufacturers of succinic acid

The global market for succinic acid in terms of revenue was estimated to be worth \$182,8 million in 2010 and is expected to reach \$496,0 million by 2016, growing at an annual growth rate of 18,7 % from 2011 to 2016. Currently, 35.000 tons of succinic acid are processed annually, though estimations predict a rise to 2.000.000 tons per year in 2020.

Europe and North America dominate the global succinic acid market and together both of them account for 66 % of the global succinic acid demand in 2010. Asia-Pacific is expected to be the fastest growing market in the near future owing to the rapid advancement and increasing demand from key countries such as China and India. In 2010, Europe dominated the global succinic acid market, accounting for 35 % of the overall consumption. America and Asia are the second and third largest succinic acid consuming regions, accounting for 31% and 28% of the overall market as presented in figure 1.4.

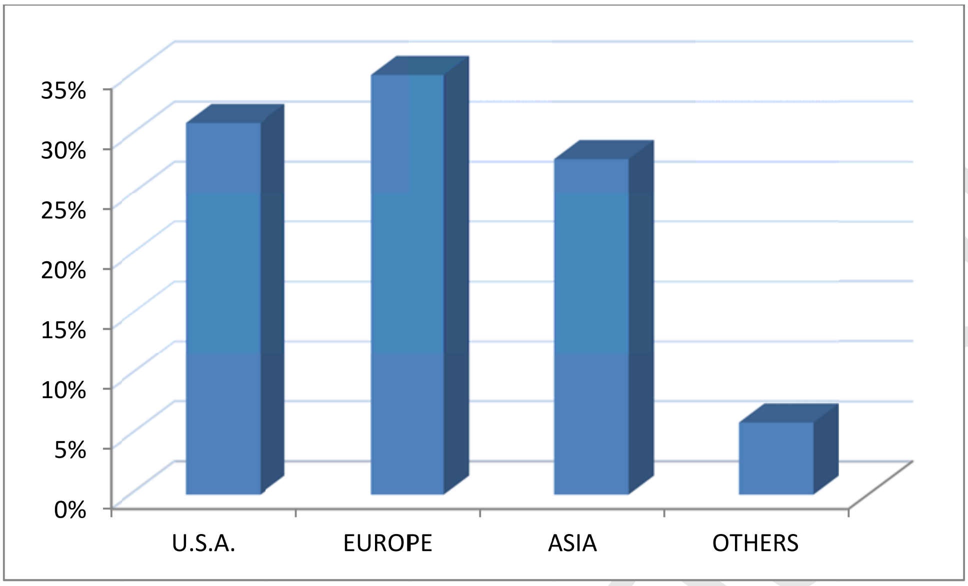


Figure 1. 4. Succinic Acid Market 2010 [39,40,41]

Since biobased succinic acid demand is increasing rapidly, many industries are showing strong interest in the production of biobased succinic acid and its derivatives. Market participants are continuously focusing on gaining market share and improve profitability.

1.2.1 Bioamber Inc.

BioAmber is the world's first and only dedicated biobased succinic acid company. The company's proprietary technology platform combines industrial biotechnology, an innovative purification process and chemical catalysis to convert renewable feedstocks into chemicals .The company is producing bio-succinic acid, PBS and they are currently finalizing the piloting of their technology to convert succinic acid into butanediol and Tetrahydrofuran (THF). BioAmber's bio-succinic acid is 97 % biobased, as it has been certified by the United States Department of Agriculture. The characteristics of their biobased chemical for industrial use are presented in table 1.6.

Table 1.6. BioAmber's succinic acid chemical properties [42]

Appearance	Powder Color white
Odor	Odorless
pH (1% in water)	2.4 – 2.8
Melting point	184 - 192°C
Kst, Pmax	Kst = 51 bar m/s - Pmax = 7,4 bar
Min. Flammability Energy	> 1.000 mJ
Min. Flammability Temp. (cloud)	620°C
Water solubility	Moderately soluble

BioAmber has developed a fermentation and downstream method to produce bio-succinic acid using raw materials from agriculture or forestry, as an alternative to petroleum derivatives. Their main raw materials are glucose or sucrose and CO_2. The biobased production process is based on small sugar requirement than most other renewable products need, because 25 % of the carbon in its biosuccinic acid originates from carbon dioxide. Moreover, there are no by-products such as ammonium sulphate since there is a 100% recycle of ammonia. Production steps are shown in figure 1.5.

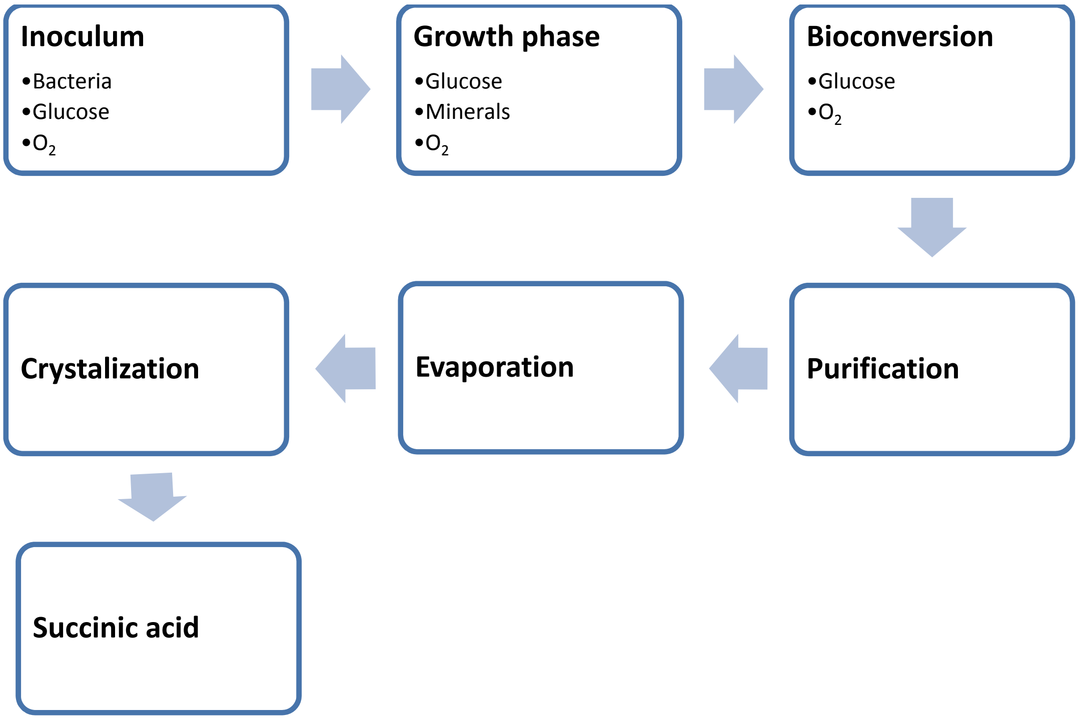


Figure 1.5. Bio-Succinic and production process [42]

The company has a demonstration plant in Pomacle in France producing bio-succinic acid at an industrial scale of 3.000 MT/year, since January 2010. The production is going under a commercial scale of a 350.000 l fully automated pilot fermentors. The facility is integrated into an existing bio-refinery that supplies the bio-succinic acid plant with glucose, carbon dioxide, steam, ammonia and process water.

BioAmber expects to establish 3 production plants worldwide for bio-succinic acid production. The first one would be in Sarnia, Ontario (Canada). The facility will have initial capacity of approximately 17.000 MT/year of bio-succinic acid and is expected to be operational in 2013, able to reach a total capacity of 34.000 MT/year, while up to year 2017 70.000 MT/year. Its feedstock will be corn. The second plant is going to be established in Thailand with an annual capacity of 65.000 MT of bio-succinic acid. The plant is expected to be operational in 2014 using cassava and sugar cane feedstock. The last one facility to be built pursuant to BioAmber's will either be in North America or Brazil, with a target annual capacity of 65.000 MT.

BioAmber's 350.000 liter fermenter in Pomacle, which started operating on January 2010, has now produced 221 tons of bio-succinic acid. The company has supply agreements for the sale of over 84.000 tons of bio-succinic acid and derivatives over the next five years, of course, coming from its planned succinic acid facilities in Sarnia and Thailand. The company estimates its succinic acid will be cost-competitive with oil price as low as $35/ barrel of crude oil and corn price at $6.50/bushel.

1.2.2. Myriant Corporation

Myriant Technologies LLC [43] was formed in June 2009 by BioEnergy International LLC and has already developed proprietary fermentation technology, through the commercial production of D (-) lactic acid. Currently, Myriant expands production including succinic acid, fumaric acid and malic acid. Generally, it is a company focused on the development and commercialization of proprietary biocatalyst technology for conversion of renewable feedstocks, into high value biobased chemicals, cost competitive with petrochemicals.

Myriant has developed a new process for the production of succinic acid that it is still demonstrated on a pilot scale producing ton-sized samples. Myriant has created a microbial platform for the manufacture of high value specialty chemicals competitive to that petroleum based. The production of chemicals from renewable feedstocks requires the use of microbes to convert sugars contained in the biomass into desired products. In particular, the company has developed a novel system that transforms genetically microbial hosts through the chromosome and not just the cell wall, making the resulting organism much more stable at large scale production. The patented process used, depends on lower cost feedstock (sugar instead of oil), milder and less expensive operating conditions (consume less energy) and require lower capital investment because there are fewer production steps.

While Myriant's initial commercial production of succinic acid will rely on first generation fermentation technologies for conversion of biomass containing readily accessible sugars to high value products, the company is also trying to develop advanced methods that consume cellulosic biomass. Myriant has developed core science and engineering competencies to support the development of robust, economically viable processes for the recovery of fermentable sugars from cellulosic feedstocks.

Concerning cellulosic technology, specially designed microbial systems convert different sugars into various high value specialty chemicals. Carbon dioxide generated in the production is consumed during specialty chemical production. Lignin byproduct from the sugar separation is burned as an energy source for the biorefinery or sold as an ingredient for downstream use. Water usage and fertilizer run-off are decreased for cellulosic biomass (compared to products such as corn and sugar beets). The process consumes less energy and water while wastes production is minimum. The characteristics of their biobased chemical are shown in table 1.7.

Table 1.7. Myriant's succinic acid chemical properties [44]

Color	white crystalline solid
Molecular weight	118,09
Melting point	188 °C
Boiling point	235 (1atm)
Density	1.57 g/cm^3
Solubility in water, 0°C	2.8
Solubility in water, 100 °C	121
Solubility in chloroform	Insoluble
pK1, in water at 25 °C	4.16
pK2, in water at 25 °C	5.61
Assay	99.5 wt %
Moisture	<0.5 wt %
Ash	<0.025 wt %
Pb	<2 ppm

Sulfate	500 ppm max
Cl	10 ppm max
As	2 ppm max
Fe	5 ppm max
N	10 ppm max
Unsaturated Compounds	0.2 wt % max
Packaging	25 kg poly bags 1000 kg Super Sack

Myriant has already constructed its 13.392 tons commercial succinic acid facility in Lake Providence, Louisiana. It is expected to start up its production of biobased succinic acid in 2013. The facility will be the world's largest biobased succinic acid plant and the company plans to expand it to 75.892 MT/year by early 2014. The company until now was focused mostly in D(-) lactic acid production at commercial scale since June 2008.

1.2.3 Royal DSM N.V. and Roquette Frères S.A. collaboration

Royal DSM N.V. [39] creates innovative products and services in Life Sciences and Material Sciences globally in a wide range of markets and applications including human and animal nutrition and health, personal care, pharmaceuticals, automotive, coatings and paint, electrical and electronics, life protection and housing.

ROQUETTE [45] is one of Europe’s largest starch and starch-derivatives businesses. ROQUETTE derives over 650 products from six million tons of maize, wheat, peas and potatoes. It serves customers all over the world in the food, paper/board, biochemicals, chemicals, pharmaceuticals, cosmetics and animal nutrition sectors.

The company’s production facility uses starch derivatives as feedstock, but in longer term the aspiration is to switch to second generation feedstock (cellulosic biomass). The currently biotechnology-based route, could result in up to 40 % reduction in energy requirements compared to the traditional method, and have a positive impact on reducing CO_2 emissions, as carbon dioxide is actually used in the production process.

Since 2007, Roquette has applied several patents concerning succinic acid production through fermentation. Patent FR 2925068 A1 implies a production method using *E. coli* in anaerobic conditions with CO_2 and MgO additions. Another patented investigation involves a three-step fermentation process with an aerobic fermentation step with *E.coli* and MgO, with a step of succinate ions production through anaerobic conditions and a last step of the transformation of ions to succinic acid.

In 2009, the two companies decided to join a venture regarding the production of biobased succinic acid. DSM and ROQUETTE have developed a method to produce succinic acid from starch using an innovative enzyme-based fermentation technology based on white biotechnology. The same year, they constructed a demonstration plant in Lestrem, France which has been running at full capacity. In 2010 the first testing volumes of biobased succinic production (Succinium™ project) proved that their biological route could be commercially viable. In May 2011, DSM and the French starch and starch derivatives company Roquette Frères announced that they will build a commercial scale plant for the production of bio-based succinic acid. With a capacity of about 10 ktons per year, the plant will be Europe's largest bio-based succinic acid facility. It is expected to come on stream in the second half of 2012 located in Cassano Spinola in Italy. By the end of 2011 / beginning of 2012 the facility was supposed to be scaled-up to full commercial industrial production with a capacity of about 10 ktons per year.

1.2.4. BASF, Purac, DNP and MBI companies

BASF and CSM and Purac explore a joint venture for the production of bio-based succinic acid. The companies have been conducting research under a joint development agreement on bio-based succinic acid since 2009. The complementary strengths in fermentation and downstream processing led to the development of a sustainable and highly efficient manufacturing process based on a proprietary microorganism. The companies aim for a 25.000 tons capacity fermentation production plant at the Purac site near Barcelona, Spain, with the intention to start up by 2013 at the latest [46, 47,41].

Another company that is moving toward large-scale production of biomass-derived succinic acid is DNP, formerly Applied CarboChemicals. The company has acquired the intellectual property to transform crop-based sugars into succinic acid. DNP's process for making succinic acid starts with a microbial fermentation. However, it uses a strain of *E.coli* developed at the Departent of Energy in the mid-1990s as part of the agency's Alternative Feedstocks Program.

At last, MBI established in 1981 has a history of developing biobased chemicals and agricultural feedstocks into chemicals derived from fermentation processes. In 1996, the company patented the process for the production of succinic acid from sugars and more specifically from a unique isolated bacterium. MBI scientists knowing that the rumen, one of the four compartments of the bovine stomach, was a warm, voluminous holding vat devoid of oxygen and brimming with microbes that digest and ferment an endless supply of well-masticated feedstuffs collected rumen samples and isolated a novel succinic acid producer. At this point, MBI has scaled-up the bench-top fermentation process for the production of succinic acid to a 1.000 gallon fermentation process at its pilot plant in Lansing, Mich.

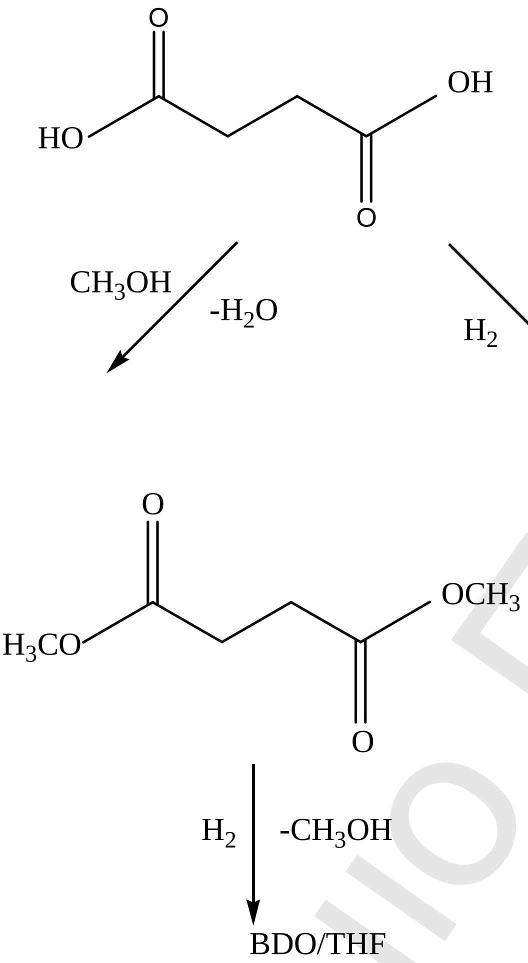
1.3. Butanediol technology and properties

Butanediol (BDO) is a raw material for a number of chemical syntheses, including poly(butylene terephthalate) (PBT) and poly(butylene succinate) (PBS) resins, used for the synthesis of films, fibers, engineering plastics and adhesives.

Butanediol (BDO) industry appears to be in the center of a technological revolution. Biological routes to BDO are being perfected which offer tremendous promise to new participants. With the global demand for butanediol estimated at 1,4 million MT in 2010, BDO's growth will continue to be derived from its almost exclusive use as an intermediate to synthetize other chemicals and polymers at an annual average rate of 4,8 percent until 2015 [48]. There is a great interest in Bio-BDO concerning the reduction of the use of petroleum-based feedstocks in light of global oil prices.

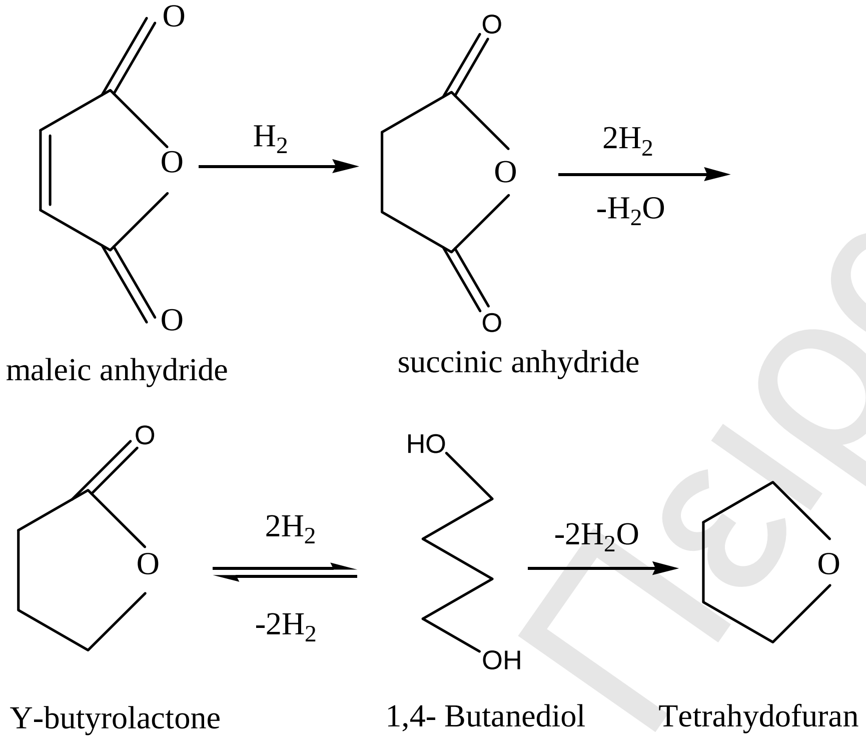
The global BDO industry has already witnessed several technological upheavals in the past. The first phase started with the development of BDO from acetylene by Dr. Reppe in the 1930s. In 1970 Mitsubishi Chemical Industries introduced the butadiene acetoxylation process. It was not until the late 1980s and early 1990s that another new technology was commercialized for BDO production, when ARCO exploited its BDO process from propylene oxide. The early 1990s saw another development, this time by the technology company/engineering contractor Davy (now Davy Process Technology) based on the esterification of maleic anhydride (made from either n-butane or benzene) with ethanol, followed by hydrogenation of the ethyl ester to diethyl succinate, then GBL, and finally BDO, typically with a tetrahydrofuran (THF) co-product (scheme 1.11). In 1998, a commoditization through technology improvements took place, including a drive to world-scale BDO plants with the introduction of SISAS maleic anhydride-based integrated BDO/THF/GBL technology, producing around 110.000 MT/year of BDO equivalents (a combination of BDO, THF, GBL, and NMP expressed as tons of BDO consumed) [48].

As innovations in BDO/THF technology continue, and improvements in the maleic anhydride-based BDO routes are still being made, new developments emerge for the production of BDO using renewable resources. As before, a whole new set of firms threatens to dramatically alter the BDO landscape through technological advances. Several of the companies are well-advanced in their construction and/or commercialization plans. Many of these developments are centered on the production of biobased succinic acid production, which can subsequently be converted to BDO/THF using conventional means, such as the Davy approach, in which the succinic acid would first be converted to the dimethyl ester and then undergo vapor phase hydrogenolysis to BDO/THF mixtures.



Scheme 1.10. Chemistry of the conversion of succinic acid to Butanediol/ Tetrahydrofuran

Other developing technologies to BDO include routes from biomass, polyhydroxyalkanoate (PHA) and direct fermentation of sugar using *E. coli* bacteria. A promising process for butanediol production is the liquid phase hydrogenation of maleic anhydride as shown in scheme 1.12. Any stage of the multistep hydrogenation of maleic anhydride to butanediol is known to be catalyzed by copper-based catalysts [9,49,50,51].



Scheme 1.11. Reaction scheme of maleic anhydride hydrogenation to butanediol/tetrahydrofuran

Another patent teaches concerning butanediol production presents a process through:

- supplying to a first hydrogenation zone a feedstream comprising maleic acid
- reacting in the first hydrogenation zone, the maleic acid feedstock and hydrogen in contact with a catalyst comprising palladium, to produce a reaction product comprising succinic acid
- supplying to a second hydrogenation zone, the reaction product of the first hydrogenation zone.
- reacting in the second hydrogenation zone, the reaction product from the first hydrogenation zone and hydrogen in contact with a catalyst comprising palladium, to produce a product stream comprising at least one of gamma butyrolactone, 1,4-butanediol and tetrahydrofuran.

BioAmber is one of the industries that supplies BDO producers with the bio-based alternative that is cleaner, cheaper and of higher purity. The company in collaboration with Mitsui&Co. is going to reach a production capacity of about 50.000 tons/year. BioAmber has exclusive license to DuPont's hydrogenation technology (figure1.6.) and it is estimated that liquid phase hydrogenation technology is the lowest cost route to BDO via succinic (bio) or maleic (petro). The used technology is less dependent on sugar price volatility, because of its high yield.

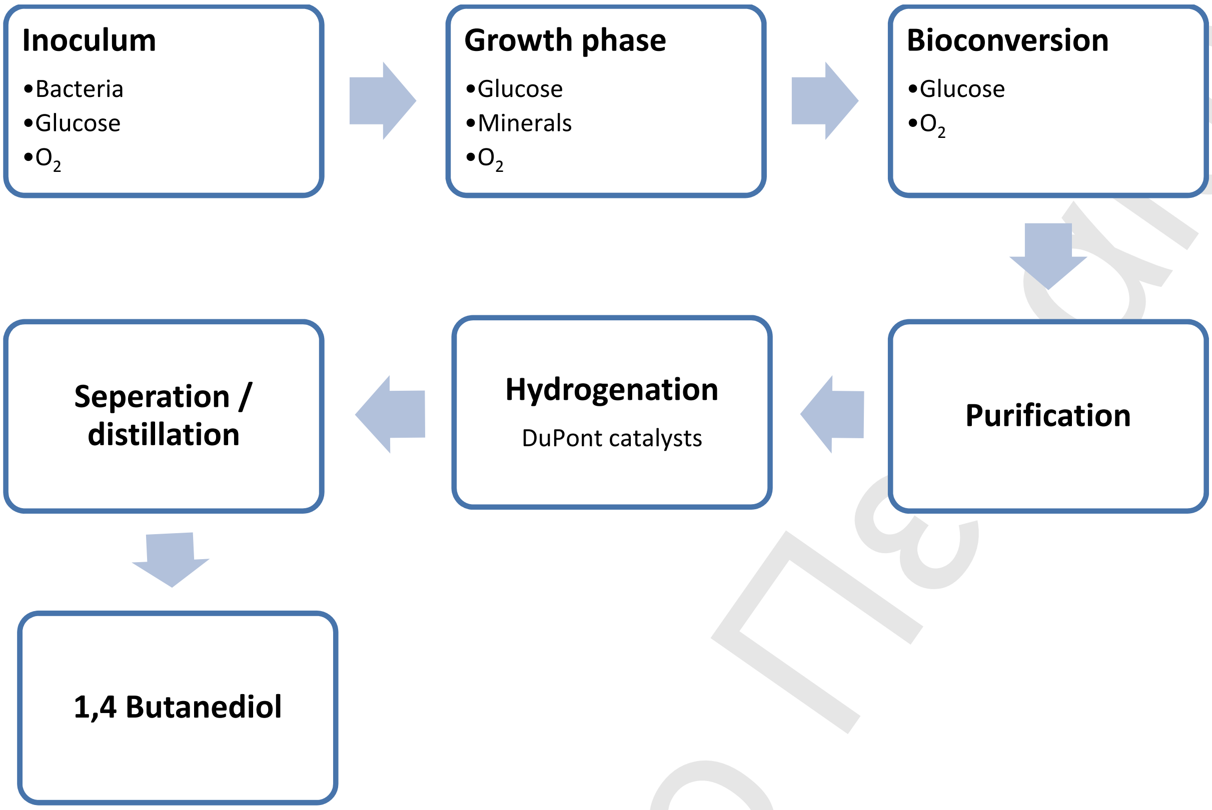


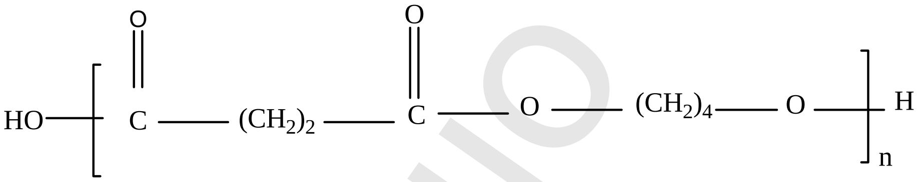
Figure 1.6. Bio-BDO production process [42]

Genomatica and Tate & Lyle is another companies' collaboration for the production of Genomatica's Bio-BDO. The Genomatica process produces the same BDO product that is currently made from a variety of petroleum-derived feedstocks, but uses 100% renewable feedstocks instead. A demonstration-scale facility has been constructed in Decatur, Illinois, for the scale-up of the Bio-BDO process. The company is ramping its process to 13.000-liter fermenters followed by an integrated downstream process for BDO recovery and purification. The company has been successfully producing at pilot scale in 3.000 liter fermentation tanks since the first half of 2010. Current feedstocks for the genomatica platform consist of refined sugars such as sucrose from sugarcane or sugar beets, and dextrose from corn or cassava, but in the current future the company plans to utilise cellulosic sugars from biomass and synthesis gas, or syngas, from municipal solid waste as the cheaper feedstocks become available. Genomatica's technology is covered by multiple patents, including US patent 80067214 B2 [52].

CHAPTER 2: DEVELOPMENT OF POLY (BUTYLENE SUCCINATE) PREPARATION PROCESSES

2.1. Introduction

Poly (butylene succinate) (PBS) and its copolymers are a family of biodegradable polyesters synthesized from succinic acid, butanediol, or other dicarboxylates and alkyldiols. PBS is a white crystalline thermoplastic with density of 1,25 g/cm^3 melting point (T_m) in the range of 90°C – 120 °C and a low glass transition temperature (T_g) of about -45 °C to -10 °C. It has generally excellent mechanical properties and processability. Like other aliphatic polyesters, it is thermal stable up to approximately 200 ^oC and because of its good biodegradability, it has attracted intense attention from both academic and industry. PBS repeating unit is as it is shown in scheme 2.1:



$$HO-\left[C(=O)-(CH_2)_2-C(=O)-O-(CH_2)_4-O\right]_n-H$$

Scheme 2.1. Poly(butylene succinate) repeating unit

PBS was currently produced by condensation polymerization of petrochemical succinic acid and butanediol, both of which are usually derived from maleic anhydride. Nowadays, poly(butylene succinate) is a particularly important, technically produced biodegradable polyester for three reasons. Firstly, succinic acid can be a biogenic monomer, i.e.it is a monomer based on renewable resources. Secondly, the rates of hydrolysis of polysuccinates are higher than those of polyesters derived from higher aliphatic dicarboxylic acids and thirdly, the melting temperature, and thus, the heat distortion temperature of PBS is the highest of all polysuccinate derivatives.

Because of its excellent mechanical properties it can be applied to a range of end applications via conventional melt processing techniques, such as injection, extrusion or blown process. New grades of PBS copolymers have also been produced with a high recrystallization rate and high melt tension, suitable for preparing stretched blown films and highly expanded foams.

PBS applications in general include mulch film, packaging film, bags and flushable hygiene products. Owing to the steady growth of the market for biodegradable plastic, the demand is expected to increase rapidly. It can also substitute for poly(ethylene terephthalate) (PET), polypropylene (PP), replace polyolefins and polystyrene in some applications, and additionally it can replace poly(lactic acid)

(PLA) in several applications. Scientists also suggest substitution potential is highest for low density polyethylene (PE-LD), high density polyethylene (PE-HD) and polyprolylene, as well as non-polymeric materials including paper, natural fibre and wood.

Figure 2.1. PBS end product applications

2.2. State of the art in homopolymers poly(butylene succinate) preparation processes

Synthetic biodegradable polymers are mostly synthesized through polycondensation or ring-opening reactions/chain extension. Polyesters have been first synthesized by W.H. Carothers in 1935. However it is difficult to synthesize high molecular weight polyesters in the initial stage. With progress of synthetic and green technology, high molecular weight polyesters are commercially available now.

Table 2.1. PBS and its copolymers production parameters

Raw Material	Catalyst	Conditions	Mw/Mn	Sources
PBS	titanium (IV) butoxide	180 ^{o}C	$\overline{M_n} =$ 59.500 $\overline{M_w} =$ 104.100	Tserki 2006 [53]
PBS	titanium (IV) butoxide	60 min 230 ◦C	$\overline{M_n} =$ 7.000	Chrissafis 2005[54]

PBS	Chain extenders : 2,2(-(1,4-phenylene)-bis(2-oxazoline) (PBOX) and adipoyl biscaprolactamate(ABC)	180–240°C chain extension for 0,5 h and at reduced pressure to 2 mmHg for 2,5 h	-	Xu 2010[55]
prePBS PBS	p-toluenesulfonic acid (p-TSA	180–200°C 2 h	$\overline{M}_w =$ 14.500 (prePBS)	Huang 2010 [56]
PBS	Biscaprolactamate as chain extender and p-toluenesulfonic acid as catalyst	Chain extension at 200–240°C under reduced pressure	-	Zhao 2007[57]
PBS	Candida antarctica lipase B	80 - 95 °C 21 h	$\overline{M}_n =$ 38.000	Azim 2006[58]
PBS	distannoxane	20 min microwave irradiation 200 W 220 °C N_2 atmosphere	$\overline{M}_w$ =23.500	Velmathi 2005[59]
PBS	tetra-n-butoxy titanate	-	$\overline{M}_n =$ 59.000	Mochizuki 1997[60]
PBS	-	-	$\overline{M}_n =$ 77.000 $\overline{M}_w =$ 141.000	Ahn 2001[61]
PBS	titanium (IV) butoxide		$\overline{M}_w$ =92.940	Rizzarelli 2004[62]
PBS	dibutyl tin dilaurate or dibutyl tin oxide	N_2 flow	-	Sonnenschein 2010[63]
PBS	distannoxane	azeotropic conditions atmospheric pressure 72 h	$\overline{M}_n =$ 117.000 $\overline{M}_w =$ 277.000	Ishii 2001[64]

PBS	$SnCl_2$, $Ti(OiPr)_4$, $Ti(OBu)_4$, $Sn(Oct)_2$, $Zn(Ac)_2$, p-toluenesulfonate (p-TS),	12 h	$\overline{M_w}$ =79.000	Sun 2007 [65]
PBS	$SnCl_2$	70 h	$\overline{M_n} =$ 24.800	Zhu 2003[66]
PBS	Bismuth based compounds	80 °C 48 h	$\overline{M_n} =$ 30.000	Lahcini 2010[67]
PBS	triflates of sodium, magnesium, aluminum, zinc, tin (II), scandium, and hafnium	80 °C	$\overline{M_n} =$ 35.000	Buzin 2008[68]
PBS	zinc acetate dihydrate		$\overline{M_n} =$ 53.000	Taniguchi 2002[69]
PBS	Sc $(OTf)_3$	160 °C 180 °C 10 h	$\overline{M_n} =$ 20.900 $\overline{M_n} =$ 30.700	Takasu 2003[70]
PBST	tetrabutyl titanate (TBT)	-	-	Du 2007[71]
Branched PBS	titanium isopropoxide	-	-	Kim 2001[72]
PBEST	Ti $(BuO)_4$	3–8.5 h 235 °C	-	Kint 2003[73]
PBSF	$Ti(OBu)_4$	200 °C 20 h	-	Nikolic 2003[74]

2.2.1. Two-step transesterification/Esterification polymerizationroute for PBS synthesis

Tsansesterification involves reaction of dimethyl succinate with butanediol in the presence of a catalyst and is the first step of the synthetic procedure followed by polycondesation in melt or solution (figure 2.2.). Butanediol and dicarboxylic ester are added at a molar ratio of 1,1:1,0 (slight excess of butanediol due to its side reaction to THF) and titanium (IV) butoxide is used as catalyst (typically at 0.05

mol % of monomers). This reaction can take place at 180 ^{o}C and may result in PBS with number-average molecular weight ($\overline{M_n}$) of 59.500 and weight-average molecular weight $\overline{M_w}$ of 104.100 [53, 75].

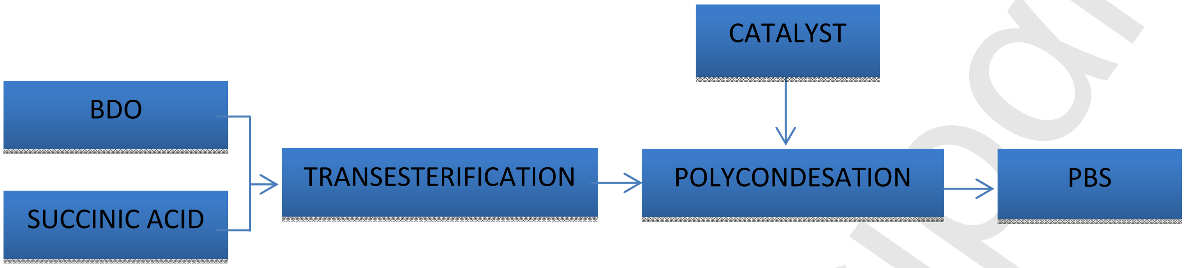


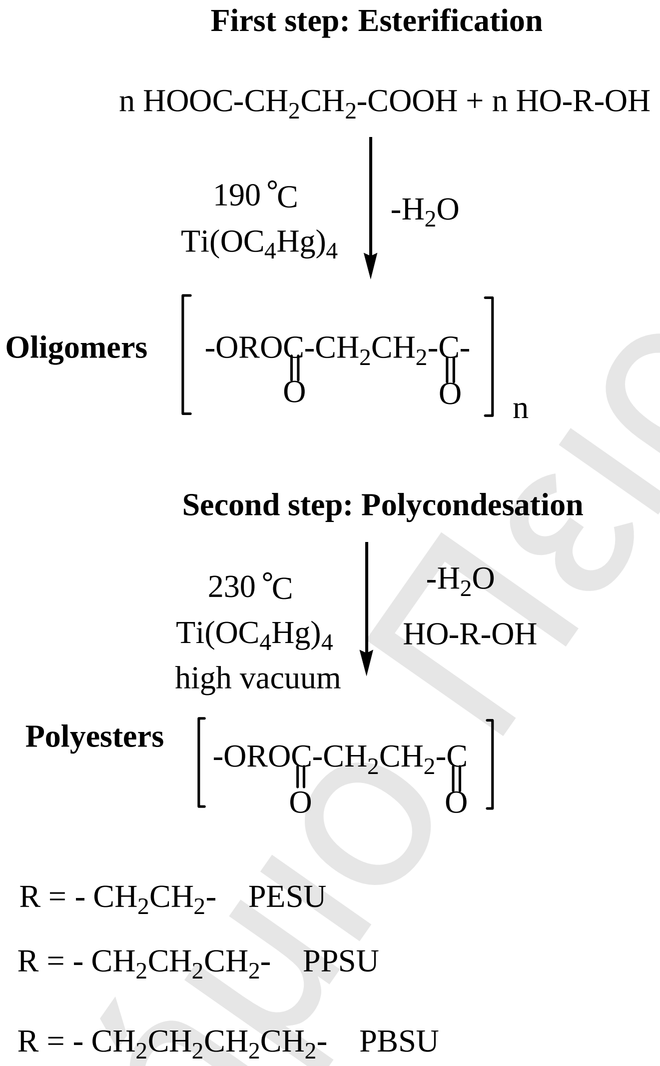
Figure 2.2. PBS production process through transesterification polymerization

A Transestrification polymerization formula of PBS from dimethyl succinate and butanediol is as it follows:

$$HO(CH_2)_4OH + CH_3OO(CH_2)_2COOCH_3 \rightleftharpoons H\,[O(CH_2)_4OOC(CH_2)_2CO]_nO(CH_2)_4OH + CH_3OH$$

Scheme 2.2. PBS synthesis through transsterification polymerization

A two-stage melt polycondensation method (esterification and polycondensation) was also studied by Chrissafis [54] using succinic acid and appropriate glycols in a molar ratio 1:1,1 and titanium (IV) butoxide as a catalyst (10,3 mol/mol succinic acid). The reaction mixture was heated at 190 ^{o}C under argon atmosphere in order to remove oxygen. PBS presented melting at 112 ◦C, glass transition at −44 ◦C and cold crystallization at 6.6 ◦C. The polycondesation followed took place under vacuum to avoid excessive foaming and to minimize oligomer sublimation. The reaction continued for about 60 min at 230 ◦C.



Scheme 2.3. Two stages melt polycondesation formula

However there is an intrinsic difficulty in synthesizing high molar mass aliphatic polyesters through the conventional polycondensation method, due to the competitive reactions of condensation and degradation, which simultaneously take place especially in the melt state.

2.2.2. Direct polymerization for PBS synthesis

Direct polycondensation is a method based on stoichiometric amounts of diacids and diols in the presence of a catalyst. Direct polymerization can be conducted in two ways: 1) direct melt polymerization of succinic acid and butanediol 2) solution polymerization of the same two reactants . Both methods have been examined intensively the current years, studying the efficiency of different temperatures and catalysts applied.

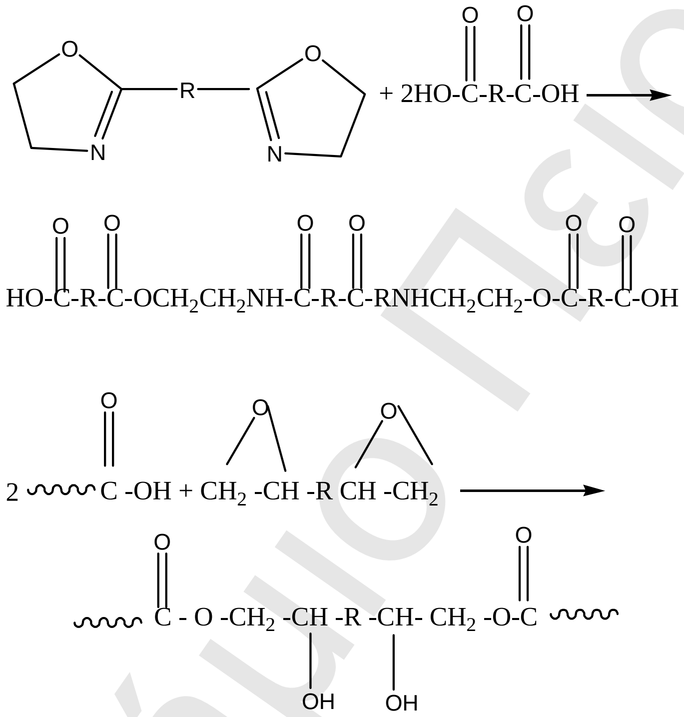
Direct melt polymerization for PBS is a direct polymerization method starting from dicarboxyl acid and diol, producing PBS of high molecular weight. Solution polymerization is a modified method of direct melt polymerization in which the monomers and the polymerization initiators are dissolved in a liquid solvent, such as xylene or decahydronaphthalene at the beginning of the polymerization reaction. The keys to obtaining high molecular weight PBS are as follows:

- The water formed during esterification must be removed from the system
- Esterification must be carried out at the proper temperature
- A sufficiently high vacuum is required to remove the butanediol and the small amount of water formed in the polycondensation stage. The Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, has applied the cold trap technique in the flow line of a PBS preparation. It is reported that the cold trap can reach −120°C and so cause the small molecular material formed in the condensation stage to condense and can keep a stable high vacuum and improve the removal of small molecular compounds. Consequently, PBS with high Mw can be prepared via this technology
- Catalysts with high reactivity and that are resistant to hydrolysis must be chosen to improve the molecular weight of PBS and to shorten the reaction time. At the same time, a thermal stabilizer and end-capping reagent are incorporated to reduce degradation during polycondensation and the following thermal processing.

2.2.3. Condensation polymerization followed by chain extension for poly(butylene succinate)

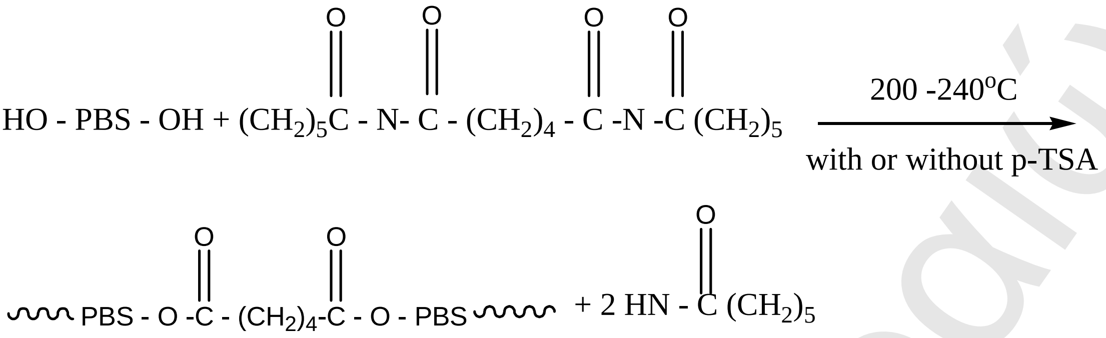
The chain extension process is a formerly developed production methodology. Compared with the direct melt condensation polymerization, an additional step is carried out to further improve the molecular weight of PBS. A chain extender with two functional groups can react with the terminal –OH or –COOH of PBS. Ideally, a chain extender molecule will couple two PBS chains. A variety of chain extenders have been investigated through years for the improvement of PBS molecular weight.

Xu et al. [55] estimated bisoxazoline as a chain extender. Extension reactions (scheme 2.4.) were carried out at 180–240^oC using 2,2(-(1,4-phenylene)-bis(2-oxazoline) (PBOX) and adipoyl biscaprolactamate(ABC) as combined chain extenders. PBOX and ABC melting points were 249^oC and 72–73^oC respectively. Prepolymer of PBS was stirred and heated under nitrogen to 180–240^oC. The chain extenders PBOX and ABC were added at molar ratios of (1/2)PBOX/–COOH¼1.0 and (1/2)ABC/–OH¼1.0, and the reaction mixture was homogeneously mixed. The chain extension was conducted at normal pressure for 0,5 h and at reduced pressure to 2 mmHg for 2,5 h. Huang [56] studied also chain extension of PBS with 2,2 -(1,4-phenylene)-bis(2-oxazoline) using p-toluenesulfonic acid (p-TSA) as a catalyst (0–0.15 wt %). There is no doubt that higher molecular weight polyesters were obtained from the catalyzed reaction than from the noncatalyzed one. However, an improperly high amount of p-TSA and a high temperature can cause branching or a crosslinking reaction. Under optimal conditions (180–200°C), PBS with an intrinsic viscosity of 0,82 dL/g in a 20 mL of chloroform ($CHCl_3$) solvent, was synthesized.



Scheme 2.4. PBS chain extension with bisoxazoline as a chain extender

Biscaprolactamate was aslo investigated as chain extender [57]. HO-terminated poly(butylene succinate) (HO-PBS-OH) was synthesized through melt condensation polymerization from adipic acid or succinic acid, with excess of butanediol (scheme 2.5.). Chain extension was carried out at 200–240^{o}C under reduced pressure. The chain extension proceeds through the elimination of caprolactam rings in the chain extenders, the adipoyl groups or the terephthaloyl groups couple the hydroxyl-terminated polyesters together and make the molecular weight of PBS increased, whether acid catalyst such as p-toluenesulfonic acid was present or not. Chain-extended PBS with intrinsic viscosity of 0.87–1.25 dL/g was obtained at 30^{o}C.



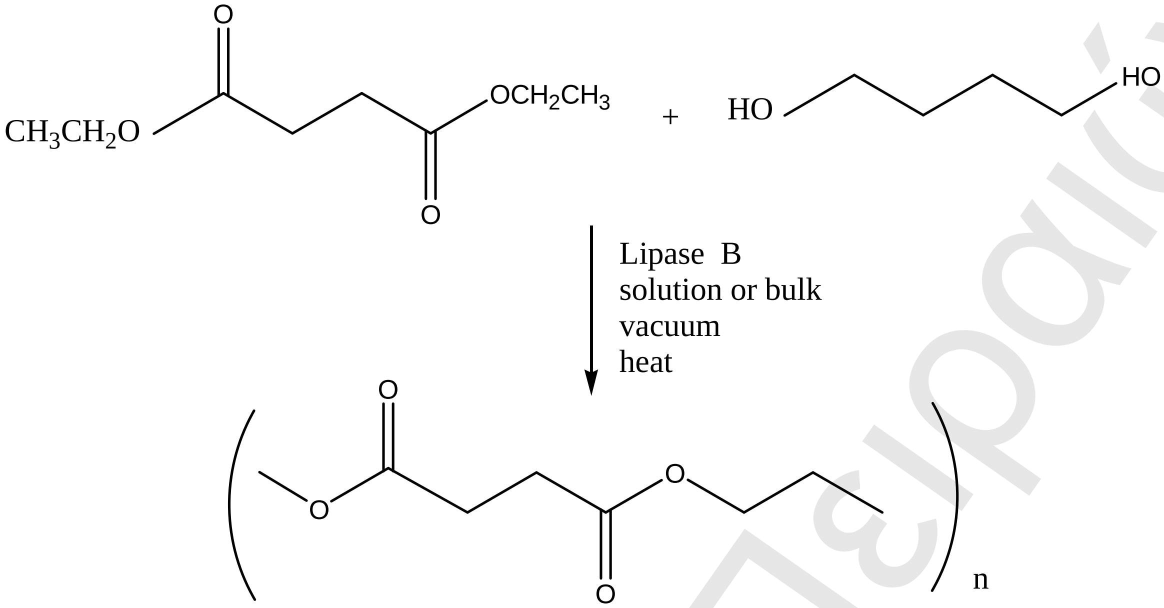
Scheme 2.5. The chain extension of HO-PBS-OH with ABC with or without the p-TSA catalyst

In this process, the polycondensation conditions are not that critical comparing to those of direct melt polycondensation. On the other hand, chain extension reactions have the disadvantage that incorporation of the chain extender can reduce the biosafety and affect the biodegradability of the end PBS product, which is important especially for packaging application.

2.2.4. Enzymatic polymerization (lipase-catalyzed) synthesis of poly(butylene succinate)

Lipase-catalyzed synthesis of PBS is a recently developed method, which is fulfilled at milder conditions without residual metal salt. Lipases are renewable catalyst with high catalytic activities both for the condensation polymerization and ring-opening polymerization of lactones under mild reaction conditions. The lipase catalyzed polymerization is considered as a new strategy for the green production of bio-based plastics [76]. PBS synthesized by lipase catalysis has a narrower polydispersity index than polycondesation methods. However, the remaining lipase may cause a problem in the following thermal processing.

In 2006, Azim et al. [58] reported *Candida antarctica* lipase B catalyzed synthesis of PBS, from the monophasic reaction mixtures of diethyl succinate and butanediol (scheme 2.6.). Lipase B (0,61 g, dried under 0,1 mmHg vacuum at 25 °C for 24 h) was added to a solution of diethyl succinate (4,00 g, 22,96 mmol) and butanediol (2,07 g, 22,96 mmol) in diphenyl ether (12,14 g). PBS with $\overline{M_n}$ of 2.000, 4.000, 8.000, and 7.000 was produced at 60, 70, 80, and 90°C, respectively. The low molecular weight was due to precipitation after polymerization for 5–10 h, limiting the growth of the polyester chain length. To maintain a monophasic reaction mixture, the polymerization temperature was increased from 80 to 95 °C after 21 h. The result was an increase in the PBS molecular weight to $\overline{M_w}$ 38.000.

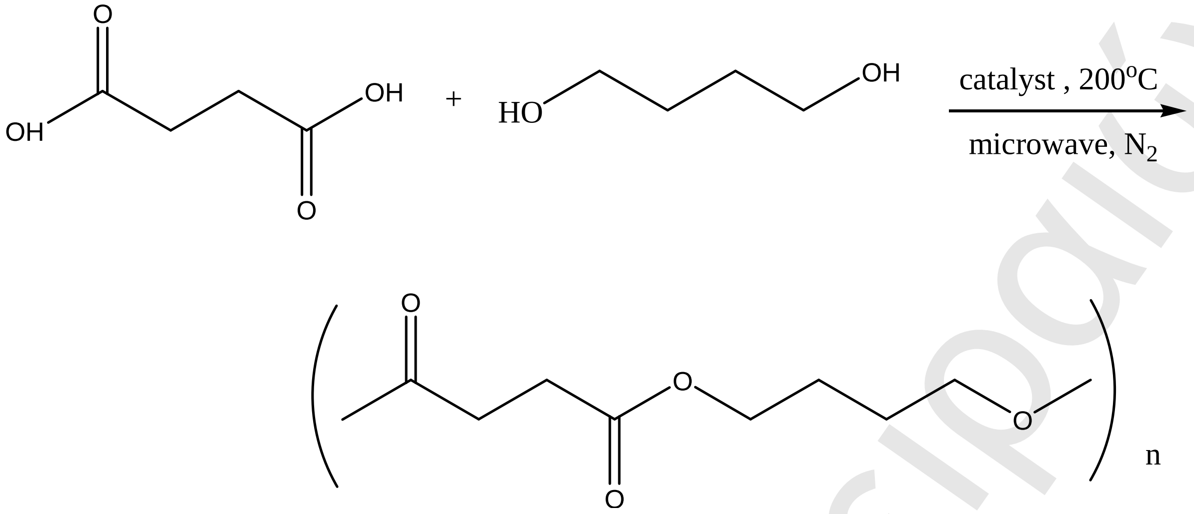


Scheme 2.6 Lipase-catalyzed condensation polymerization for PBS

Another work was that of Briassoulis according to which PBS production was made through a two steps process beginning with the production cyclic oligomer by the lipase-catalyzed condensation of dimethyl succinate and 1,4 butanediol in a dilute toluene solution using lipase from *Candida Antarctica*. The polymerization of cyclic oligomers proceeded without producing a condensation by-product, such as water and a lower alcohol, in 90^oC for 48 h. Following, a ring-opening polymerization of the cyclic oligomer took place in a more concentrated solution or in bulk with the same lipase in 120^oC for 24 h. In order to produce high-molecular-weight polyester, the ring-opening polymerization of cyclic oligomers could become a new revolutionary means of manufacturing polyesters that are now typically synthesized by a polycondensation reaction.

2.2.5. Direct polyesterification under microwave irradation

An eco-friendly method for PBS synthesis has been studied by Velmathi [59]. PBS has been produced by the direct esterification of a dicarboxylic acid and a diol using distannoxane catalyst under microwaves (scheme 2.7.).The optimum parameters were found to be a catalyst concentration of 2 mol %, a bulk polymerization method, a reaction temperature of 220 ^oC, a stoichiometry of 1:1,2 of dicarboxylic acid and diol, respectively, and a microwave irradiation time of 20 min. The PBS synthesized was obtained in 81,3% yield with a $\overline{M_w}$ of 23.500. The reaction took place under a N_2 atmosphere at a maximum microwave power of 200 W.



Scheme 2.7. Synthesis of PBS under microwave irradiation

Both melt and solution polymerization of succinic acid and butanediol were attempted. Concerning bulk polymerization, the reaction time was fixed at 20 and 30 min and with 2 mol-% of the catalyst maximum $\overline{M_w}$ 9.600 and 12.200 were obtained respectively. In the case of solution polymerization, the polymer with the maximum $\overline{M_w}$ 19.300 was formed with 2 mol-% of the catalyst in 30 minutes. Compared to the bulk polymerization, the yield obtained was low in most cases, which might be a consequence of the decalin (a non-polar solvent), which is a microwave inactive solvent resulting in a poor microwave eating effect. With an increase in the irradiation time there was an increase in Mw of the polymer obtained.

The advantages of this method, such as short reaction time, freedom of solvent, and performing under atmospheric pressure, makes it possible to synthesize aliphatic polyesters in a rapid and ecofriendly way without any solvent and under mild conditions compared to the conventional methods.

2.3. State-of-the-art in Copolymer and branched PBS preparation processes

In order to improve the properties and the biodegradation rate, PBS copolymers and branched structures have been synthesized. PBS copolymers are obtained from succinic acid or succinate, butanediol, and other dicarboxylic acids, such as adipic acid, terephthalic acid, succinic acid with substituted side groups, sebacic acid, or alkylenediols such as 1,3-propanediol, or other substituted glycols. Usually, copolymerization leads to a decreased degree of crystallinity, depressed heat distortion temperature and higher molecular weight by incorporating a suitable chain extending agent in the polymerization stage.

Branching has been also proved effective in enhancing processability in the processes involved with elongational flow, such as fiber spinning, film blowing, vacuum forming, and foaming. Branching also increases the melt strength and confers a tension-hardening property on the polymer, which is of help for uniform extension in the polymer processing, in which a high degree of orientation is required.

The production process of PBS copolymers can be through the two-step transesterification route, and the raw material inputs are butanediol and binary acid, using a high-efficiency catalyst for polymerization. Most important PBS compolymers will be described in the following section.

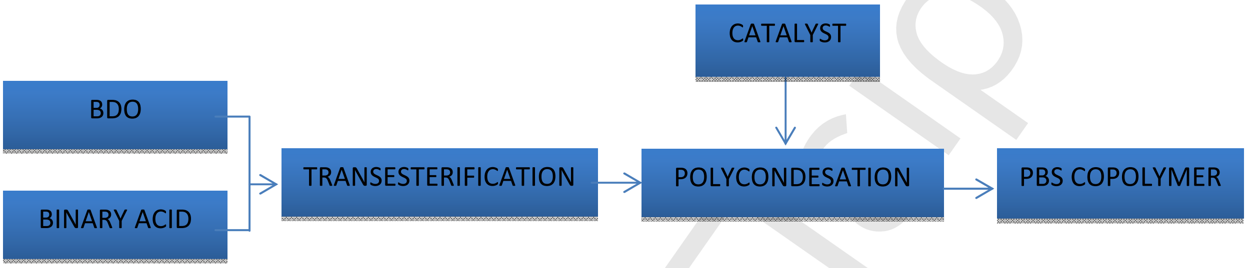
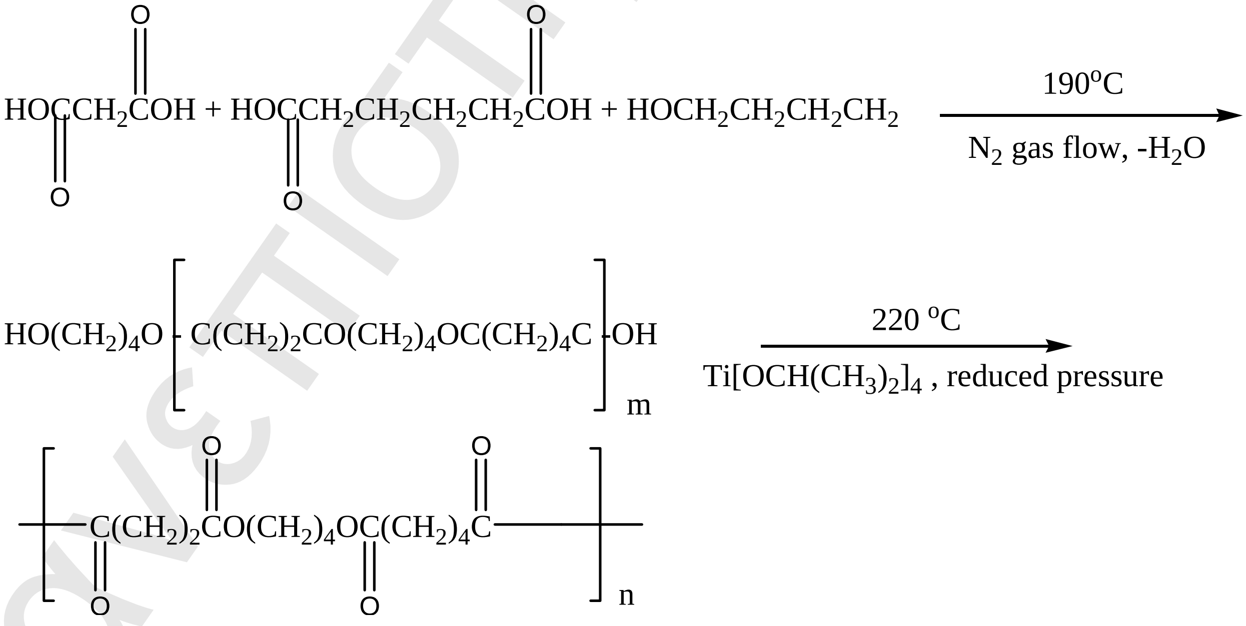


Figure 2.3. PBS copolymers production process

2.3.1. Poly (butylene succinate /adipate) copolymer (PBSA)

In 2002, Ahn et al. [61] produced poly(butylene succinate/adipate) copolymer by reacting butanediol and dicarboxylic acids under N_2 atmosphere. Esterification reaction took place for 2 h at 190°C and then the active catalyst titanium isopropoxide was added prior to deglycolization reaction which took place ar the temperature of 220°C. The structures of these copolyesters are presented in the scheme 2.8.



Scheme 2.8. PBSA copolymers synthesis

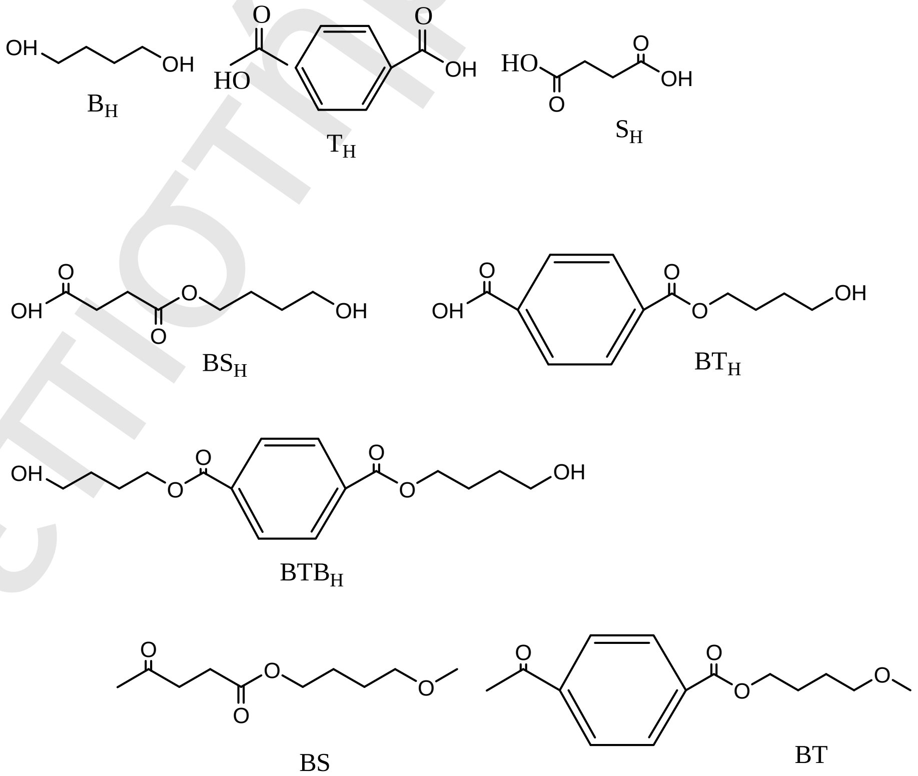
Nikolic et al. [77] obtained a two-step transesterification reaction in the melt for PBSA production. Butanediol, dimethyl adipate and dimethyl succinate were the reactants using $Ti(OBu)_4$ as a catalyst. A copolymer with a molecular weight 73.000 was attained.

High molecular weight biodegradable PBSA copolymers was also obtained from butanediol, dimethyl esters of succinic and adipic acid, with the incorporation of hexamethylene diisocyanate as chain extender. The reaction took place at at 140 °C for 1 h under nitrogen inlet [53].

Regarding properties, in the case PBSA, tensile strength decreases with the introduction of the secondary component (adipate), exhibiting a tendency similar to that of the other physical properties. PBS is the polyester with the highest tensile strength, while the copolymers of PBSA shows improved elongation [61].

2.3.2. Poly (butylene succinate-co-butylene terephthaloyldioxy dibenzoates) (PBST)

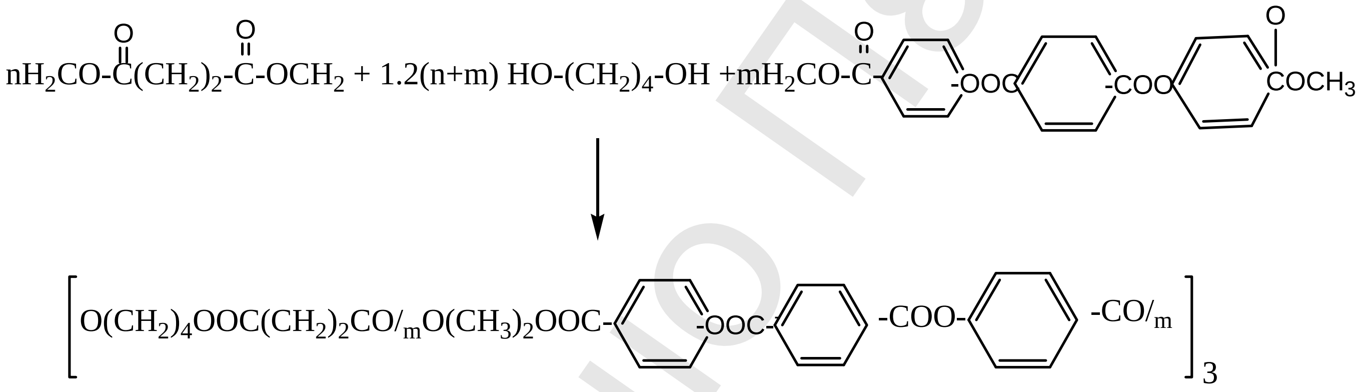
A series of liquid crystalline aromatic/aliphatic random poly(butylene succinate-cobutylene terephthaloyldioxy dibenzoates) (PBSTs) copolymers were prepared by melt polycondensation of a new mesogenic monomer dimethyl 4,40-(terephthaloyldioxy) dibenzoate (MTB), dimethyl succinate, and 1,4-butanediol, using tetrabutyl titanate (TBT) as catalyst and hexamethylene diisocyanate was used as chain extender [71].



Scheme 2.9. Chemical structires of monomers and oligomers [78]

Investigation carries out by several scientists indicated that increased temperature and excess chain extender could not only activate the chain extension reaction, but also accelerate the side reactions, such as branching or crosslinking, reducing the solubility of the products. Therefore, ameliorated chain extension need to be conducted to reduce the possibility of crosslinking. Chain extension temperature and chain extender content were both factors affecting chain extension reactions. Therefore, a stable chain extension method by decreasing the reaction temperature and reducing the diisocyanate content was introduced.

In the process of PBST synthesis using a small excess of the diol over the diesters, is presented below in scheme 2.10.



Scheme 2.10. PBST copolymers synthesis

Moreover Xu et al. [55] in order to increase the thermal and mechanical properties of PBS prepared a series of potentially biodegradable liquid crystalline aromatic/aliphatic random copolyesters by melt polycondensation of MTB, dimethyl succinate, and butanediol. A two-step polycondensation technique was followed as well and the $\overline{M_w}$ values of the copolyesters were in the range of 24.400 to 53.600 g/mol. It was also found that T_m, crystallization behaviour and hydrolytic degradation rate of the copolyesters decreased gradually with increasing the MTB content. In comparison the elongations at break increased remarkably with increasing MTB content.

Honda et al. [78] synthesized PBST and revealed the effect of aromatic block unit on their enzymatic degradation under a lipase, and the biodegradability of PBST copolyester could be tailored with increasing the population of aliphatic butylene succinate block.

2.3.3. PBS copolymers filled with talc

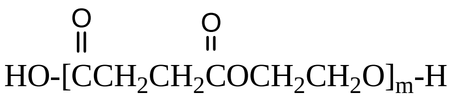
Talc is a highly functional additive that enhances key properties of numerous resins. In addition to being a cost-effective filler, talc can effectively provide antiblocking, reinforcement, and improved barrier properties. During polymer processing, talc, as the softest mineral, minimizes equipment wear. It also decreases mold shrinkage, and improves end product machining.

Plastics exhibit increased stiffness, reduced mold shrinkage, improved heat stability and lower material costs when filled with the appropriately sized talc. Impact strength can be maintained when the particle size is carefully controlled to a 1 to 2 micron, ultrafine median particle size while maintaining a minimum top size. In addition to size, talc particle shape and particle aspect ratio can be used to further optimize these properties. Talc with an aspect ratio of 10 to 1 when melt compounded with a homopolymer will provide a 250 percent increase in flexural modulus too. Polyester gel coat barrier properties are improved with the addition of fine ground, platy talc. Talc also functions well as a nucleating agent during melt compounding.

The block copolymers can be produced by any well known polymerization or copolymerization procedure including sequential addition of monomer techniques, incremental addition of monomer technique or coupling technique. The talc may be added with the polyester reactants before polyester is prepared or the talc may be blended with the polyester after its preparation by conventional techniques [80]. It has recently been discovered that the incorporation of talc filled into thermoplastic polyesters which have been modified by the incorporation of a butadiene-based modifier, causes the degradation of the polyester. So these talc filled thermoplastic polyester compositions degrade during the mixing of the composition as well as during further processing operations such as extrusion and injection molding [80, 81].

2.3.4. Other copolymers

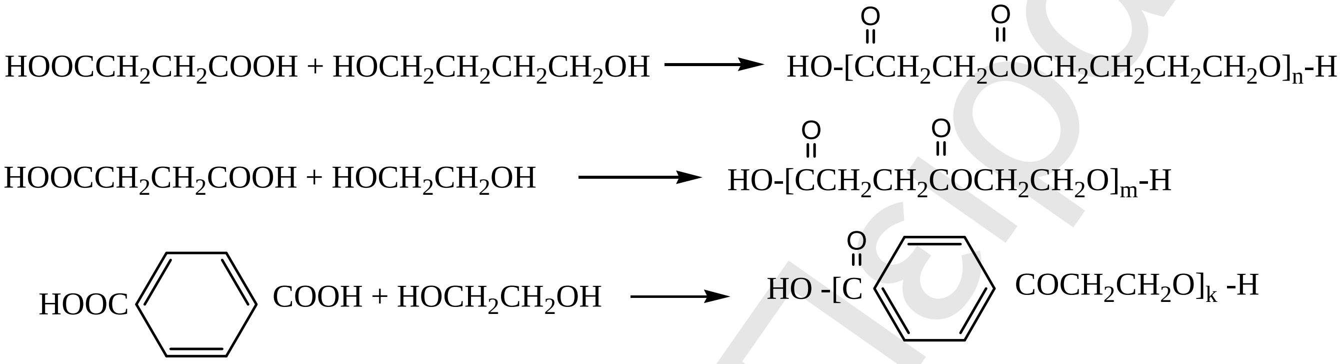
A new copolyester poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate) (PBEST), was synthesized via direct polycondensation from three prepolymers of butylene succinate, ethylene succinate and ethylene terephthalate. PBEST has excellent elongation behavior and biodegradability at a certain composition. Particularly, its elongation at break is around 1200 % when PBES contains 78 mo l% of PES and 22 mol % of PBS .



$$HO\text{-}[\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_2O]_m\text{-}H$$

Scheme 2.11. PBEST structural unit

All the synthesized copolyesters have an intrinsic viscosity ranging from 0,62 to 0,86 dl/g (in $CHCl_3$ at 20 ± 0,1 °C) within a reaction time range of 3–8,5 h. In particular, a longer reaction time is needed for polyesters with a higher content of poly(ethylene-succinate) PES, indicating that Ti $(BuO)_4$ catalyst was not so highly efficient for the synthesis of copolyesters containing high content of (PES) prepolymer although it was a very efficient catalyst for synthesis of other copolyesters.



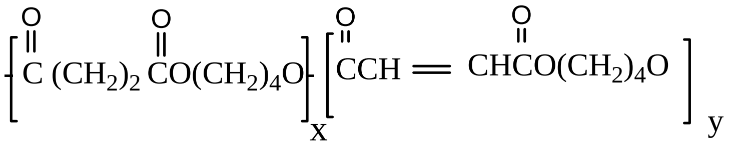
$$\mathrm{HOOCCH_2CH_2COOH + HOCH_2CH_2CH_2CH_2OH \longrightarrow HO\text{-}[\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_2CH_2CH_2O]_n\text{-}H}$$

$$\mathrm{HOOCCH_2CH_2COOH + HOCH_2CH_2OH \longrightarrow HO\text{-}[\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_2O]_m\text{-}H}$$

Scheme2.12. PBEST synthesis [82]

For the synthesis of PBEST copolyesters, the reaction temperature reached around 235 °C, which was above the temperature of the ester bond cleavage in prepolymers, thus leaded to the possibility of ester exchange reaction. Meanwhile, a long reaction time was also assumed to be in favor of the ester exchange reaction [82].

Another copolymer based on PBS is the aliphatic poly(butylene succinate-co-butylene fumarate) (PBSF), which is synthesized by a two step transesterification reaction. PBSF copolymers show slightly higher melting and crystallization temperatures than the corresponding homopolyester, PBS. The incorporation of double bonds into the polymer chains makes them stiffer which in turn has the effect of increasing the melting temperature. All the copolyesters are less thermally stable than PBS homopolymer and increasing content of fumaric residues the stability is decreased. The trend was opposite in air. Although the copolyesters are less stable than PBS, their stability increases with increasing fumarate content. Also, the copolyesters are more stable in air than in nitrogen as a result of thermal degradation inhibition because of the oxygen and that these inhibitory reactions take place at the double bonds. The highest biodegradability was observed for the copolyesters containing 5 and 10 mol% of fumarate units.

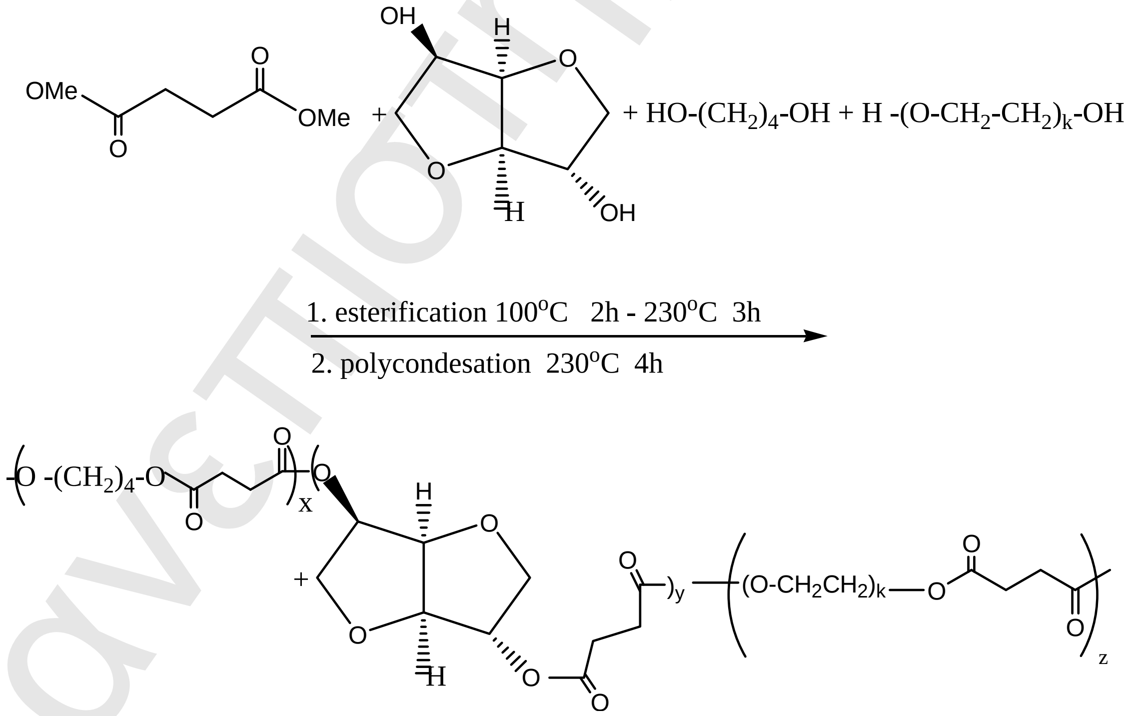


$$\mathrm{\left[\overset{O}{\overset{\|}{C}}(CH_2)_2\overset{O}{\overset{\|}{C}}O(CH_2)_4O\right]_x\left[\overset{O}{\overset{\|}{C}}CH=CH\overset{O}{\overset{\|}{C}}O(CH_2)_4O\right]_y}$$

Scheme 2.13 High molecular PBSF

Starting from the dimethyl esters (dimethyl succinate and dimethyl fumarate) and butanediol with a diol excess and $Ti(OBu)_4$ as a catalyst. Reaction temperature was maintained under vacuum at 200 °C for 20 h [75]. In order to prevent reaction on the double bond of the fumaric acid, the transesterification reaction was carried out at 200 °C for longer periods of time, 12– 20 h depending on the composition of the reaction mixture. The key to the successful synthesis of high-molecular weight aliphatic polyesters is the combination of a highly effective catalyst and the proper choice of polymerization conditions, such as the reaction temperature and reaction time, which would diminished side reactions on the reactive double bonds of the fumaric moieties.

Another aliphatic copolyester poly(butylene succinate -co- isosorbide succinate -co- polyethyleneoxide succinate) (PBxIyEzS) was synthesized by the two-stage melt polycondensation method composing of esterification and polycondensation in the presence of dimethyl succinate (DMS), 1,4-butanediol (BDO), isosorbide (ISO) and poly(ethylene glycol) (PEG). PBxIyEzS copolyesters synthesized from three different diol moieties (BDO, ISO and PEG) have high molecular weights and they are suitable to be used in fields where flexible materials are needed. Biodegradable copoloyesters based on renewable resources were successfully synthesized by the transesterification and polycondensation in the melt from poly(butylene succinate), poly(ethylene glycol) and isosorbide. Compared to pure PBS, the PBxIyEzS copolyesters showed lower crystallization temperature, melting temperature and crystallinity while a significant increase in glass transition temperature with increasing isosorbide content [83].

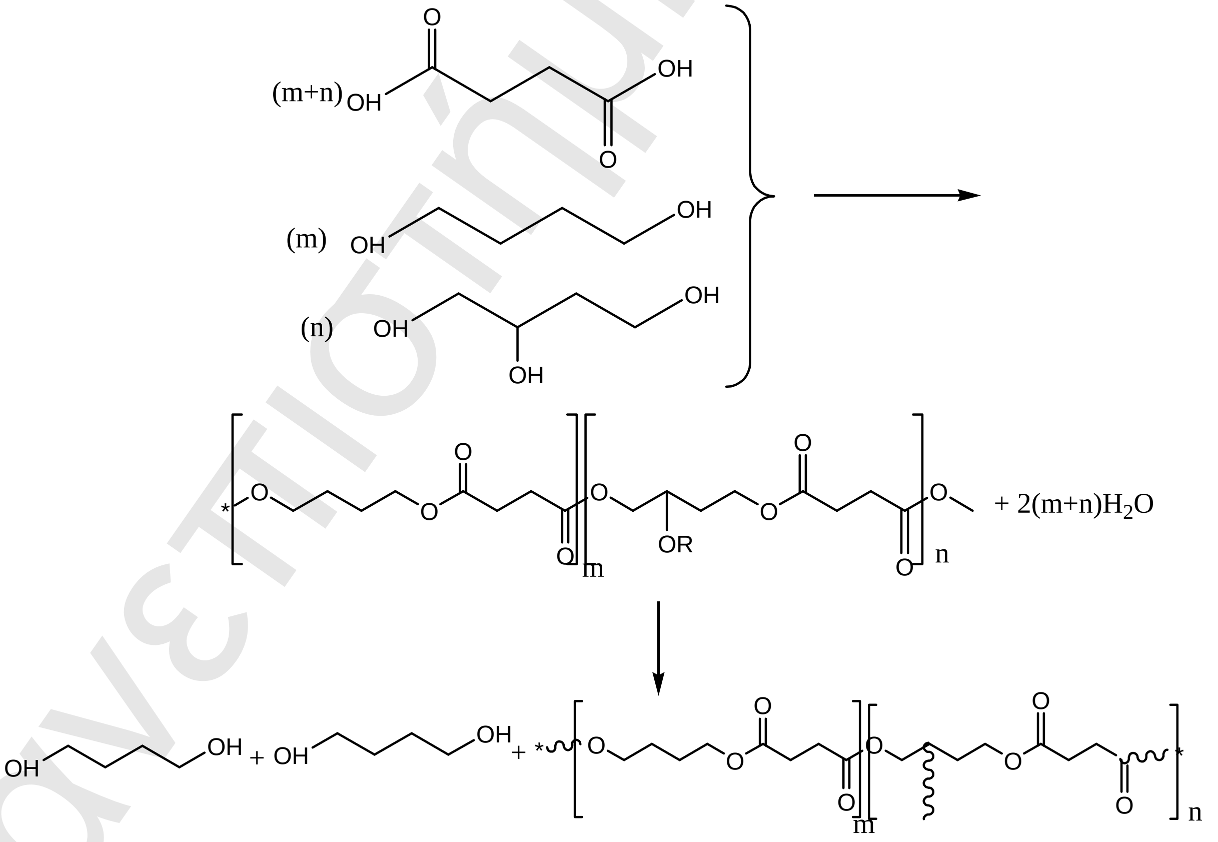


Scheme 2.14. Synthesis route of $PB_xI_yE_zS$

2.3.5. Branched PBS

Kim et al. [72] produced long branched poly(butylene succinate), by introducing a branching agent, trimethylol propane (TMP) and titanium isopropoxide as a reaction catalyst. It was found in the same study that T_m is slightly decreased as the content of modifier is increased. However, crystallization temperature (T_c) was notably decreased with increasing the modifier content. The reduction in T_m and T_c results from the fact that chain branching reduces molecular regularity and retards crystallization. The number-average molecular weight is decreased with TMP content while the weight-average molecular weight is increased.

Long-chain branched PBS was also synthesized, using 1,2,4-butanetriol as a long-chain branching agent and $Ti(OBu)_4$ as a catalyst. The results of the research showed that with the increasing of 1,2,4-BT segments, the crystallization temperatures and glass transition temperatures increase slightly, while the relative crystallinity degree decreases gradually. The viscoelastic properties of branched PBS under shear flow were different from the linear PBS. The complex viscosities of long-chain branched PBS increased in comparison with those of linear PBS. Concernigng $\overline{M_n}$ it was first increased gradually and then decreased slightly with the increasing of 1,2,4-BT segments [84].

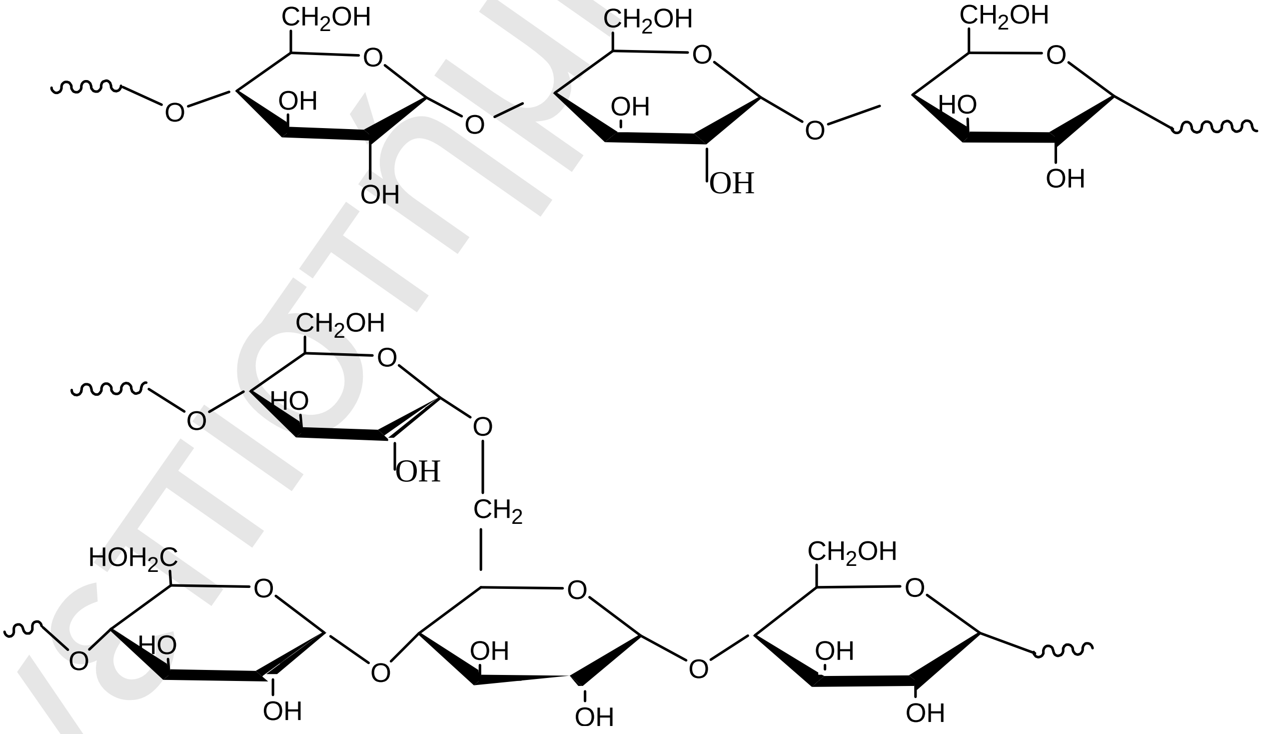


Scheme 2.15. Synthesis of long-chain branched PBS [84]

2.3.6. PBS blends and nanocomposites

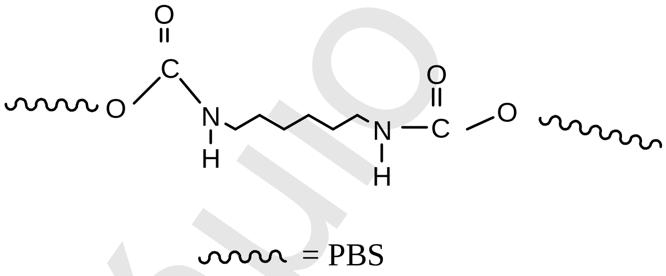
Starch is totally biodegradable, environmentally friendly and low cost material. Nevertheless, since starch is highly sensible to water and has relatively poor mechanical properties compared to other petrochemical polymers, its use is limited. So the solution is to blend it with other synthetic polymers (scheme 2.16). A lot of research work deals with the development of blends of starch with synthetic biodegradable polymers. These blends present several advantages [85].

The blending process is low cost compared to the cost of the development of new synthetic materials. These kinds of blends are intended to be more biodegradable than traditional ones. PBS was blended with granular corn starch [86]. Increasing the starch content, the elongation at break and the tensile strength were decreased. On the contrary, the addition of starch fillers significantly improved the degradation rate. The studies of blends of starch with aliphatic polyesters (PCL, PBS, and PHBV) showed in all cases that only a modest level of starch is possible. To improve compatibility between the starch and the aliphatic polyester, a compatibilizer was used. It contains an anhydride functional group and was incorporated onto the polyester backbone. The tensile strength obtained for such blends was close to that of synthetic polyester, only with a small amount of compatibilizer [87].



Scheme 2.16 PBSA – starch blend

For certain applications, biopolyesters cannot be fully competitive with conventional thermoplastics since some of their properties are too weak. Therefore, to extend their applications, these biopolymers have been formulated and associated with nano-sized fillers, which could bring a large range of improved properties (stiffness, permeability, crystallinity, thermal stability). Sinha Ray et al. [88] first reported structure and properties of PBS/clay nanocomposites (PBSCN) obtained by melt intercalation. Other studies [88, 89] investigated the effect of the organoclay type on the composites structures and properties. High molecular weight PBS was synthesized by a coupling reaction with a chain extender, namely the hexamethylene diisocyanate ($OCN-C_6H_{12}-NCO$), resulting in urethane moieties and terminal hydroxyl groups. After many researches testing metal-based catalysts (dibutyltin dilaurate $Sn(Bu)_2(Lau)_2$, titanium(IV) butoxide $Ti(OBu)_4$ and antimony(III) oxide Sb_2O_3) for the esterification reaction, $Sn(Bu)_2(Lau)_2$ appeared to be the most appropriate one. Sinha Ray et al. also reported PBSA-based nanocomposites. Cloisite30B appeared the most suitable nanofiller for PBSA-based nanocomposites prepared by melt intercalation.



Scheme 2.17. Formation of urethane bonds in high molecular PBS

A last, rice husk (RHF) and wood flour (WF) are two of the agro-materials that can be used as reinforcing fillers in biodegradable polymer biocomposites. RHF is an agricultural waste material generated in rice-producing countries, especially in the Asian, Pacific, and North American regions. Most of this rice husk is used as a bedding material for animals and the industrial applications of this material are limited. Therefore, the use of rice husk in the manufacture of agro-material–filled biodegradable polymer biocomposites is attracting much attention because of the potential biomass energy. With increasing agro-flour content in the PBS biocomposites, there was a more rapid decrease in the tensile strength, notched Izod impact strength, and percentage weight loss of the biocomposites by bacteria and fungi during the natural soil burial test. Agro-flour–filled PBS biocomposites are environmentally friendly and degradable materials that can be considered as alternatives to conventional plastic materials for packing, injection-molded, and disposable products [90].

2.4. Catalysis in poly(butylene succinate) preparation

PBS synthesis is mainly carried out with titanium (IV) isopropoxide, titanium (IV) isobutoxide or titanium (IV) n-butoxide [60,91,92]. It is generally accepted that titanium and specially tetrabutoxytitanium is the most active catalyst for transesterification polymerization [93]. Mochizuki et al. [60, 91] synthesized PBS with $\overline{M_n}$ up to 59.000 using tetra-n-butoxy titanate as a catalyst and polyphosphoric acid as a thermal stabilizer. Using titanium (IV) isopropoxide, Ahn et al. [61] produced PBS with $\overline{M_n}$ of 77.000 and $\overline{M_w}$ of 141.000. Rizzarelli [63] starting from dimethyl succinate and butanediol in the presence of titanium (IV) butoxide, obtained high molar mass polymers with a Mw 92.940.

Sonnenschein et al. [63] also studied PBS synthesis through polycondensation of succinic acid with butanediol using dibutyl tin dilaurate or dibutyl tin oxide as catalyst .Samples of 1.000 g/mol or 2.000 g/mol were synthesized under N_2 flow. Germanium and antimony metal oxides can also display desirable catalytic efficiency, when they are associated with hydroxy acids, which are acting as chelating agents. However, this catalytic system exhibits lower efficiency compared to a titanium one [53,75]. These catalysts appear to be less effective than alkoxides, but have the advantages of being water stable and soluble in ethylene glycol at room temperature. The ability of metal oxides to catalyze PBS transesterification was clearly improved by the presence of hydroxy acids. Nevertheless, when the concentration of these compounds became too high, the efficiency of the catalytic mixture began to decline. This decrease in efficiency is linked to the quantity of hydroxyl acid added since the insertion of hydroxy acid units in PBS chains decreases the proportion of ‘‘active’’ hydroxyl PBS end-groups that play a dominant role in transesterification [94].

Ishii et al. [64] reported one-step synthesis of PBS by distannoxane-catalyzed polymerization of succinic acid and butanediol in a two-phase system of solvent (decalin) and molten polymer under azeotropic conditions at atmospheric pressure. When the reaction time was extended to 72 h in the presence of 0.001 mol% of catalyst, PBS with Mn of 117.000 and Mw of 277.000 was obtained.

At the National Sun Yat-sen University, researchers [65] examined the effect of different catalysts, such as $SnCl_2$, $Ti(OiPr)_4$, $Ti(OBu)_4$, $Sn(Oct)_2$, $Zn(Ac)_2$, and p- toluenesulfonate (p-TS), on the molecular weight of solution-polymerized PBS. Among these catalysts, $SnCl_2$ showed the most promising result, producing PBS with a $\overline{M_w}$ of 79.000 after a 12 h reaction. Utilizing a new water trap that contains a 4-Å molecular sieve, Zhu et al. [66] synthesized PBS with $\overline{M_n}$ of 24.800 after polycondensation for 70 h with $SnCl_2$ as a catalyst and dimethyl benzene as the solvent and water-removing agent.

Takasu et al. [95] gave emphasis to rare earth triflates as catalysts for the room temperature direct polycondensation of dicarboxylic acids. Bismuth based compounds as catalysts can lead to a $\overline{M_n}$ up to 30.000 after abulk polymerization at 80 ^oC for over 48 h [67].

Buzin et al. [68] is another one who examined polycondensations with the triflates of sodium, magnesium, aluminum, zinc, tin (II), scandium, and hafnium. Polycondensations and model experiments proved that most triflates catalyzed the formation of tetrahydrofuran from butanediol above 100 °C and that the highest $\overline{M_n}$ values were achieved with Bi (OTf)$_3$. At temperatures of 80 °C the number-average molecular weights up to 35.000 and at temperatures up to 120°C $\overline{M_n}$ <10.000 were not obtained. PBS homopolymer produced by the ordinary melt polycondensation with zinc acetate dihydrate as the catalyst, obtained a number-average molecular weight of 53.000 with a polydispersity in $\overline{M_w} / \overline{M_n}$ of 1.9. The T_m and T_g were determined to be 114 ^oC and -34^oC, respectively [69].

In order to reduce side reactions and consumption of energy, low temperature polycondensation methods have recently attracted increasing interest. For instance, 2,2-dibutyl-1,3-stannepane reacts at room temperature exothermically with succinyl chloride, but the $\overline{M_n}$ of the resulting PBS grades was low, due to rapid crystallization of the oligoesters. The most versatile approach yielding any kind of aliphatic polyesters with moderate to high $\overline{M_n}$ is the polycondensation of diols with dicarboxylic dichlorides catalyzed by pyridine at temperatures <20 °C. Yet, this approach is particularly expensive and not suited for upscaling. Ueda and coworkers claimed that high molar mass PBS maybe obtained, when butanediol and succinic acid, were stirred with or without catalyst at 120 °C, followed by heating to 200–210 °C in refluxing decalin. The addition of decalin had the purpose to remove the liberated water azeotropically and to maintain a biphasic reaction mixture, so that the polycondensation proceeded at the highest possible monomer (and oligomer) concentration. However it is demonstrated that the combination of the ‘’Ueda method’’ with non-trace Bi catalysts, represents a satisfactory approach to the preparation of PBS. This conclusion is supported by the finding that the commercial PBS has an inherent viscosity of only 0.40 dL/g, when measured under the conditions of this work.

Recently, new catalysts have been developed that are based on rare-earth metals, such as Sc(OTf)$_3$ or Sc(NTf$_2$)$_3$. These catalysts are capable of achieving the bulk polycondensation of methyl ester of succinic acid with butanediol under mild conditions (35 ^oC). Moreover, these catalysts can be recovered and reused by solubilization in chloroform and extraction with water. Polycondensation times at such temperatures remain very long (>50 h), and the final number average molar mass of $\overline{M_n}$, ranging from 5.000 to 12.000 g/mol is relatively low [53,75]. Takasu [70] demonstrated that Sc (OTf)$_3$

can catalyze not only the esterification of PBS but also etherification as a side reaction, which depends on the chain length (methylene number) of the diols. The catalyst makes it possible to prepare biodegradable polyesters, having a $\overline{M_n}$ over 10.000 even at 35 °C. The polycondensation at 160^{o}C and 180 °C for 10 h gives a PBS polymer with a $\overline{M_n}$ of 20.900 and 30.700 respectively, even in the presence of 0,1 mol % catalyst. Direct polycondensation using the recovered catalyst gave PBS with a $\overline{M_n}$ of 14.300.

In summary, metal ranking is Ti > Ge > Zr> Sn > Hf > Sb > Bi. Despite the fact that Ti-based catalysts are highly efficient, they should be used with caution due to the important degradation reaction that they induce. That was particularly outlined by the carboxylic acid end-groups contents, yellowness indexes and reduced viscosities, which were measured upon ageing. Residual metals in these materials are difficult to remove, because of strong metal-ester interactions. These metals can cause undesirable effects on the environment upon material disposal, limit polymer use in applications such as electronics, and may be unacceptable components of medical materials. Furthermore, the combination of high reaction temperatures and organometallic catalysts can lead to monomer/ polymer decomposition reactions and, hence, discoloration and decreased product molecular weight.

2.5. Industrial production of poly(butylenes succinate)

The first attempt for PBS synthesis was made in 1931 by Carothers. The PBS obtained was of low molecular weight, less than 5.000, and was weak and brittle. In 1993, Showa High Polymer produced high molecular weight PBS under the trademark Bionolle, which was synthesized via melt condensation polymerization followed by a chain-extension method [96]. However chain-extended PBS was not suitable for some applications. Thereafter, researchers and companies attempted to manufacture high molecular weight PBS via direct melt polycondensation. In 2003, Mitsubishi Chemicals introduced GS Pla. After three years, Hexing Chemical, Anhui produced PBS through direct melt polycondensation and in 2007, Xinfu Pharmactical built a PBS production line with one-step polymerization technology [97]. The major manufacturers of PBS and its copolymers are listed in Table 2.2.

Table 2.2. PBS and copolymers producers

Manufacturer	Product
Hexing Chemical, China	PBS and copolymers
Bioamber	Renewable modified PBS (mPBS)
Xinfu Pharmaceutical, China	PBS, PBSA
Jinfa Tech, China	PBSA
Anqing Hexing Chemical Co , China	PBS
BASF, Germany	Ecoflex
Eastmann, USA	East Bio
Showa, Japan	Bionolle
Mitsubishi Chemical, Japan	GS Pla
Mitsubishi Gas chemicals, Japan	Iupec
Nippon Shokubai, Japan	Lunare
Ube, Japan	ETERNACOLL 3050
Ire Chemical, Korea	Enpol
SK Chemicals	Skygreen

2.5.1. Showa Highpolymer - Bionolle

Showa Highpolymer, part of the Showa Denko Group in Japan was the first company to produce a commercial biodegradable PBS polymer with the trade name Bionolle. Grades of Bionolle are poly(butylene Succinate) (#1000 series), poly(butylene succinate adipate copolymer) (#3000 series) and poly(ethylene succinate) (tentatively #6000 series). Showa Denko has selected Myriant as its global supplier of biosuccinic acid as a raw material [98].

These polymers were first produced through polycondensation reaction of butanediol with aliphatic dicarboxylic acids and in case of need for higher molecular weights, coupling reaction was carried out with coupling agents acting as chain extenders (e.g. hexamethylene diisocyanate). Chain extension of HO–PBS–OH with diisocyanate can produce PBS with a relatively high molecular weight in a range of about 20.000-200.000 and weight average molecular weight ($\overline{M_w}$) at about 40.000-1.000.000 [99,100].

The esterification reaction can be carried out at 160°C - 230°C for 5-16 h preferably under nitrogen gas atmosphere. Then, transesterification is carried out at 170°C - 230°C for 2-16 h under a decreased pressure. However in view to the reaction rate and the prevention of decomposition, it is preferable to perform the reaction at 180°C - 210°C under high vaccum state [99,100].

Bionolle is a semi-crystalline polymer and flexible. The polymer was designed to have the processibility of polyethylene with physical properties similar to those of poly(ethylene terephthalate) [88]. It has high flexibility, excellent impact strength, and thermal and chemical resistance. It can be processed easily and is the best choice to blend with poly(lactic acid). Showa Denko produces also Bionolle derived from biobased succinic acid. Using more than 60 % of starch as a raw material, the end product Bionolle Starcla is a biobased environmentally friendly polymer, which returns to nature because it is completely biodegradable. Physical properties of Bionolle are shown in Table 2.3 below.

Showa Denko K.K's Bionolle family of biodegradable plastics have received numerous "green" certifications from associations across the globe including the "GreenPla" label by the Japanese BioPlastics Association (JBPA), the "OK Compost" mark by AIB-Vincotte (AVI) and the Belgian based certification and screening body, for its capacity to completely biodegrade.

Table 2.3. Physical properties of Bionolle and its grades [96,98]

	Units	PBS			PBSA	
Density	g/l	1.260			1.230	
Heat of combustion	KJ/g	23.6			23.9	
Heat deflection temperature (at 0.45 MPa)	°C	97			69	
Crystallinty	%	35-45			41	
Melting point (Tm)	°C	114-115			114	
Glass transition	°C	-32			-45	
Grade		1001MD	1020MD	#1903	3001MD	3020MD
MFR (190°C, 2.16kg)	g/10min.	1.5	25	4.5	1.4	25
Crystallization temperature	°C	75	76	88	50	53
Flexural modulus	MPa	660	640	690	320	340
Tensile yield strength	MPa	32	34	39	19	19
Tensile break strength	MPa	57	21	35	47	34
Tensile elongation	%	700	320	50	900	400
Structure	-	Linear		Long chain branch	Linear	

Bionolle is commercial available until 1994. Showa Highpolymer constructed a pilot plant with a capacity of 10 tons/year in 1991 and a semi-commercial plant with a capacity of 3.000 tons/year in 1993. In 2002 Showa doubled its capacity to 6.000 tons/year [60]. Showa HighPolymer sells Bionolle for € 3,50 per kilo and expects this price to go down only marginally to € 3,00 per kilo [98]. Since the raw material has the most influence on the cost price, Showa claims that the percentage of costs attributed to the feedstock will increase (from 50 % in 2003 to 85 % in 2030). Showa's projections are in sharp contrast to the expected decrease in raw material cost (both in absolute terms and relative to total costs) which is expected for the bio-based route.

2.5.2. SK Chemicals – SkyGreen

SK Chemicals, Korea is also reported to have a small plant producing PBS and PBSA with the trademark SkyGreen BDP (Table 2.4). SkyGreen is a series of aliphatic polyester and aliphatic/aromatic copolyester that is degraded into water and carbon dioxide by microorganisms. This product has been mainly developed on the basis of the SK Chemicals PET technology and there is no other chemical linkage than ester in its molecular structure [101].

Table 2.4. Physical properties [102]

Density	1.27 g/cm^3
Tensile strength break	26 MPa
Elongation break	70%
Flexural modulus	2150 MPa
Heat distortion temperature (0.455MPa)	74^{o}C
Melting Point	110 °C

2.5.3. Mitsubishi Chemical – GS Pla

Mitsubishi Chemical produces bio-based PBS named as GS Pla®[60]. Succinic acid obtained through glucose fermemtation processes, butanediol and lactic acid are used as raw materials, which through a direct dehydration polycondensation are transformed to PBS [103].

The main GS Pla characteristics are safety, workability and molding properties. GS Pla is aliphatic polyester available for various molding processes, like inflation, extrusion, injection and blow. Moreover it can present great compatibility with other biodegradable resins. As far as degradation is concerned, the polymer can be decomposed into water and carbon dioxide by microorganisms in the natural environment. Physical properties of Bionolle are shown in Table 2.5.

Table 2.5. Physical properties of GS Pla grades [104]

Physical properties	GS Pla grades			
	FZ91P	AZ91T	AD92W	GZ95T
Density g/cm^3	1,26	1.26	1.24	1.51
Glass transition temperature ^{o}C	-22	-24	-36	-24
Melting point ^{o}C	115	110	88	110
Tensile strength MPa	40	55	50	33
Tensile elongation at break %	250	450	800	5
Flexural modulus MPa	650	550	300	1.800
Izod impact strength kJ/m	9	10	35	5

2.5.4. Bioamber-Modified PBS (mPBS)

Bioamber using biobased succinic acid as a raw material produces renewable modified poly(butylene succinate) plastic (mPBS). This revolutionary modified PBS has better performance than other biodegradable polymers sold today, with heat resistance above 100 ^{o}C, excellent strength properties and the ability to be processed in existing production equipment. Bioamber is the first company to commercialize PBS with renewable content above 50 % [105].

These new composites are engineered and designed at the molecular level using BioAmber's proprietary technology to meet end-user requirements for high performance, biodegradable plastics. The uniformity, performance and processability of mPBS in existing equipment has been confirmed by a number of end users, with applications ranging from foodservice cutlery and coffee cup lids to plates, bowls, straws and stirrers, as well as non food contact applications such as razor handles, sheets, films and fibers.

Among the basic chracteristics and benefits of mPBS are:

- High heat distortion temperature, up to 110°C (230°F)
- High strength and stiffness
- Good ductility and strength
- Great processability
- Drop-in existing production equipment
- Injection molding and extrusion grades
- Meets global biodegradability standards
- Grades that can be used in food contact
- Flexibility to use petroleum and/or renewable raw materials

2.5.5 Other industries

Anqing Hexing Chemical Co. Ltd.is a high technology enterprise producing PBS based on biological technology. It can be applied for fields such as package, tableware, cosmetics bottle, medicine bottle, one-off medical supplies, agricultural films, pesticides, fertilizing slow-release materials and biological medical macromolecule materials etc [106].

IRE is another big company producing PBS with the trademark EnPol. These polymers are produced through the polycondensation reaction of glycols and dicarboxylic acids with IRe's self-developed catalyst and process technology [78]. EnPol polymers are stable in the atmosphere, but biological decomposition commences when exposed to bacteria or fungi and moisture. Living micro-organisms transform EnPol polymers into water, carbon dioxide and biomass. In addition, EnPol polymer completely decompose in normal composting conditions without any harmful by-products, and harmless to the environment at every stage of decomposition process. Ire produces several EnPOl grades such as:

- EnPol G4560 [PBS] whose mechanical property can be a adjusted by changing melting flow index (M.F.I) depending on the purpose of product in polycondensation process
- EnPol G4560J [PBS]. Its T_m and specific gravity are same as those of G4560 but its MFI is higher than that of G4560.

These polymers can be applied as disposable goods (cup, knife, spoon, fork, razor, straw, golf tee), films (compost bag, trash bag, shopping bag, packaging film, shrink film, blister film, etc.), agriculture and horticulture (mulch film, plant pot, rope or string, clip, etc), fishing gear (fishing net, Fishing trap, rope, fishing line) and containers (tray, food containers, bottles, shampoo, detergent, beverage).

China Materials Holding Ltd produces high molecular weight PBS from butanediol and succinic acid in the presence of catalyst through one of the two production methods: the chain extension process or the direct polycondensation process patented by the Technical Institute of Physics and Chemistry of the Chinese Academy of Sciences IPCCAS. They initially engaged IPCCAS to investigate into the feasibility of constructing a 20.000 tones per year PBS production facility adopting its direct polycondensation process in 2008. In July 2009, they entered into a letter of intent with IPCCAS for the licensing of this patented process to construct a 20.000 tones per year PBS production facility, as well as setting up a joint research laboratory to research into new PBS formulations and potential applications. Subsequently in December 2009, the company entered into a formal technology licensing agreement with IPCCAS under which they were granted a non-exclusive license to use the relevant PBS resin polymerization technologies in their PBS production facilities and our 500 liter PBS laboratory facility adopting the IPCCAS process [107].

CHAPTER 3: CHARACTERIZATION AND CRITICAL PROPERTIES OF POLY(BUTYLENE SUCCINATE)

3.1. Methods for poly(butylene succinate) molecular weight determination

3.1.1. Gel permeation chromatography

Molecular weight of synthesized PBS can be determined using gel permeation chromatography (GPC). Polystyrene is used as a standard with a low polydispersity in order to make a calibration curve and chloroform as an eluent at a flow rate ranging between 0.8 mL/min - 1 mL/min [108, 109]. GPC can be performed at 40 ^{o}C [64], 35^{o}C [53, 75] or room temperature. Shah et al. [110] used hexafluoroisopropanol (HFIP) as an eluent and the molecular weight was measured relative to poly(methyl methacrylate) (PMMA) at 40^{o}C.

Another way to measure the weight-average molecular weight ($\overline{M_w}$), number-average molecular weight ($\overline{M_n}$), and molecular weight distribution ($\overline{M_w}/\overline{M_n}$) for polymers is size exclusion chromatography (SEC) using SEC columns with a refractive index detector. Chloroform was used as the eluent at 1.0 mL/min in this case too. The SEC system is calibrated with polystyrene standards having a narrow molecular weight distribution [76]. Except chloroform for SEC analysis, tetrahydrofuran stabilized with hindered phenol can also be used as mobile phase at the velocity of 1.0 mL/ min. However PBS presents a poor solubility in THF.

Lahcini in his study [67] in order to estimate the molecular weight of the obtained polymers, he has taken into account that several research groups reported that direct comparison with polystyrene standards in chloroform overestimates the real molecular weights by 50–80 % (depending on chemical structure and mass range). This overestimation corresponds to correction factors in the range of 0,55–0,67. When the SEC measurements of three PBS samples were evaluated via the universal calibration method it was found that the direct calibration with polystyrene causes an overestimation of $\overline{M_n}$ and $\overline{M_w}$ by 80–100 %.

The difference between several researchers and their results can only be explained by the different starting points used for the evaluation of the elution curves. In the case of polycondensation the maximum of the frequency distribution is usually the dimeric species (regardless if linear or cyclic). Therefore, polycondensates contain a high molar fraction of oligomers, which is important for the calculation of $\overline{M_n}$ even when their mass fraction is low. If the evaluation of the elution curve begins with the mass of the dimer (around 400 Da) with a mass of 2000 Da or with a mass of 5000 Da may result in a variation of Mn by a factor of 10, whereas the influence on $\overline{\mathrm{M_w}}$ is small. Therefore, $\overline{\mathrm{M_n}}$ values of polycondensates published without definition of the mass range used for their calculation are absolutely meaningless.

Moreover, the difference of the molecular weight detected by GPC from that calculated by the hydroxyl number is due to different methods of the measurements. Molecular weight calculated from the hydroxyl number is the absolute molecular weight. But $\overline{\mathrm{M_n}}$ and $\overline{\mathrm{M_w}}$ detected by GPC are relative molecular weight. The number-average molecular weight Mn of PBS can also be calculated from intrinsic viscosity [η] values, using the Berkowitz equation: $\overline{\mathrm{M_n}} = 3{,}29 \times 10^4\, [\eta]^{1{,}54}$ [93].

In a study done by Kim et al. [72] it is proven that concerning branched PBS the number-average molecular weight ($\overline{\mathrm{M_n}}$) decreased with increasing branching agent content, while the weight-average molecular weight ($\overline{\mathrm{M_w}}$) increased. This means that the polydispersity index increased with increasing branching agent content. Molecular weights and polydispersities of the PBSA and PBSA/starch blends were determined by GPC using chloroform. PBSA solutions of varying concentration were used to prepare a calibration curve of molecular weight. However, because of the insolubility of starch in chloroform, only the PBSA component of the blends could be detected in the chromatograms [86]. In the following table Mn, Mw and Mw/Mn results from several bibliographical sources are presented.

3.1.2. End group concentrations analysis

To determine the number of moles of a polymer, the analysis method must respond equally to each molecule without regard to its chain length. The monomer molecules at the ends of the chain must in some way be different from the chain itself. For a linear polymer (i.e., one in which there are no bonds, called crosslinks, between the chains) every molecule has two end groups, which may be identical or different. If the end groups can be analyzed, the number of polymer molecules may be calculated using simple stoichiometric relationships. Using this end group analysis method Mn can be easily determined.

Carboxyl end-group content (COOH) can be determined by a titration method using chloroform as a solvent at room temperature, NaOH in methanol as a standard and phenol red as indicator. For hydroxyl groups (OH) the polyester is dissolved just in chloroform [54]. An equation used for the calculation of the carboxylic acid end-groups content (CC) is:

$$\mathrm{CC}\ (\mu_{eq}/g_{polym}) = [(V_{eq}\ \mathrm{x} C_{NaOH)}/m_{polym}]\ \mathrm{x}10^3$$

where, CC is the carboxylic acid end –groups content, Veq is the volume of the solution, C_{NaOH} is the NaOH concentration and m_{polym} is the molar mass of the polymer.

It is has been proved that carboxylic acid end-groups content can be increased with the quantity of catalyst contained in the polymer [94] and decrease constantly with time at all temperatures [111]. Carboxyl end groups are reducing only by esterification reaction, but it is interesting to note that after the first polycondensation hour a plateau in the carboxyl end-group values is almost reached.

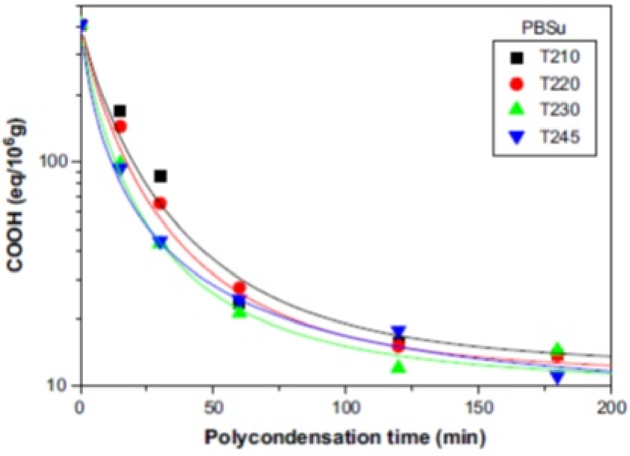


Figure 3.1. Variation of the COOH content with time during polycondesation of PBS at different temperatures [93]

As far as hydroxyl groups are concerned, an initial abrupt reduction takes place at the beginning of the polycondensation reaction, while afterwards this reduction levells off. This reduction was more pronounced at higher temperatures. The values of the hydroxyl end groups do not show the plateau observed in COOH end groups instead they continuously decrease.

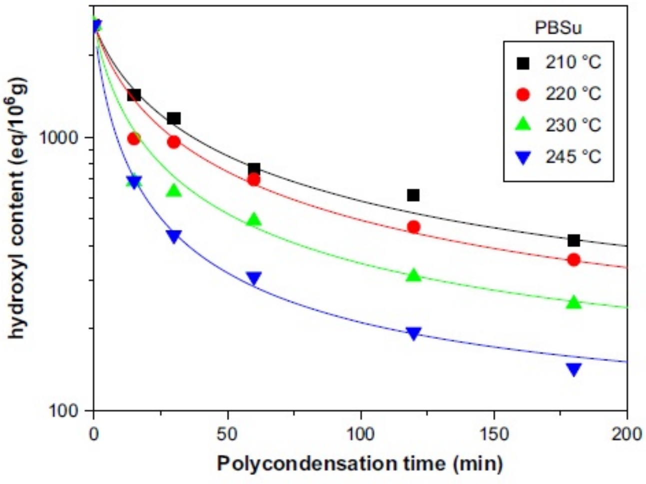


Figure 3.2. Variation of the OH content with time during polycondesation of PBS at different temperatures [93]

Velmathi et al. [59] produced PBS polymers and analysed their end group using ^{1}H-NMR spectroscopy. The results showed a peak corresponding to the the main polymer chain, and a very small triplet at 2,5 ppm corresponding to the methylene protons of the succinic acid end group. This observation suggested the formation of COOH end groups of the polymer chain. A very small broad peak at 3,3 ppm was also found and assigned to terminal –OH protons. A multiplet at 3,6 ppm corresponds to the O– connected methylene protons of the end group and a multiplet at d 1,6 ppm was assigned to the methylene protons. These peaks are similar to butanediol peaks confirming the presence of a diol end group.

Chrissafis et al. [54] estimated -COOH 79 eq/10^{-6} and -OH 58 eq/10^{-6} end groups and proved also that end groups and mainly carboxyl groups can accelerate the thermal decomposition of PBS polyesters. On the other hand concering enzymatic degradation, it is known that the initial weight decrease is much lower for the carboxyl end-capped PBS in comparison with that of the hydroxyl end-capped PBS. This fact suggests that the carboxyl end-capping with bulky group efficiently retards the enzymatic reaction, while the hydroxyl end-capping has no effect [20].

3.1.3. Solution viscosity

Solution intrinsic viscosity ([η]) measurements of PBS are usually performed in a suitable viscometer at 25^{o} C in chloroform solvent. An equation then for the calculation is the Solomon–Ciuta equation

$$[\eta] = [2\ \{t/t_0 - \ln(t/t_0) - 1\}]^{1/2}/C$$

where c is the concentration of the solution, t is the flow time of solution and t_0 is the flow time of pure solvent [93].

The intrinsic viscosity of PBS homopolymer is in the range of 0,14 to 0,64 dl/g, depending on the amount of –OH and –COOH terminal groups [55]. Chain-extended PBS presents an intrinsic viscosity of 0.87–1.25 dL/g [57] and copolyesters between 0.46 and 0.83 dl/g. The values of the Newtonian complex viscosity (measured at 130 ^{o}C) which could also be used as an indicator of the molecular weight of the polyesters, are in the range from 13,4 to 250 Pas [77]. Yashiro [112] and Lahcini [67] have measured the inherent viscosity using dichloromethane as a solvent instead of chloroform.

It is widely documented that a high degree of branching in a polymer backbone provides enhanced solubility, lower viscosity and lower crystallinity, for the case of symmetric chains that readily crystallize, than a linear polymer of equal molecular [η] of a branched chain to a linear chain, conventionally denoted as g', is employed as below

$$g' = \frac{[n]_{branched}}{[n]_{linear}}$$

The value of g’ is easily determined using the procedure of Hudson et al., where a multi-angle laser light scattering (MALLS) detector and a viscosity detector are coupled with SEC [113]. The value of [η] branched is measured directly using the viscosity detector and [η] linear is calculated using the Mark–Houwink relationship $[\eta]_{linear}=KM_w^a$. The parameters, K and a, are the Mark–Houwink constants for a linear polymer. For a linear chain, g’ and g are equal to 1 and decrease as the level of branching increases [114].

3.2. Melt flow index

PBS is a typical thermoplastic and can be processed via various methods, such as extrusion, injection molding, film blowing, fiber spinning, and thermoforming. However, its processability depends on rheological properties. PBS is a shear-thinning melt, which demonstrates decreasing viscosity with the increase of shear rate. For film blowing, strain-hardening, the tensile viscosity improves with the tension rate, is preferred for a stable process line. To obtain the goal, long branches were introduced into the PBS polymer chain.

The traditional melt index test (ASTMD 1238) is widely used in the plastics industry to characterize polymer processability. Melt flow index method is now used in a wide variety of thermoplastics. It comprises measurement of the mass flow rate of a polymer through an orifice of specified dimensions under prescribed conditions of load, temperature, and position of a driving piston in the plastometer barrel.

However, the results must be interpreted cautiously, because polymers are usually processed under conditions that are far removed from those of the melt index test and the method suffers from several severe shortcomings. First, the measured flow rates are not always steady-state values. The actual results may be very sensitive to the details of the measurement procedure, especially for low melt index polymers. Second, and more important, melt index values cannot be expected to be very useful predictors of processability since most commercial thermosplastics are shear thinning and are actually processed at much higher shear rates than those prevailing during the meltflow index measurement [115].

Variations of the procedure have been devised for different polymers and processability ranges. That makes easier to relate the melt index of a polymer to some characteristics of its molecular weight distribution since the latter is presumably the unifying factor whereby relations can be established between polymerization conditions and product properties.

The flow rate of PBS and its copolymers is determined as a function of applied load with the mass flow rate expressed in gram mass per 10 min measured at 190 ^{o}C. Some measures of melt flow indexes are presented in table 3.2.

Table 3.1. Melt flow index measures for Bionolle

PBS grade	MFR (g/10min)	Bibliographical sources
Bionolle 1020	29	Showa High Polymer Co. Ltd [98] Toyoseiki Co. Ltd. [116]
Bionolle 1003	5	
Bionolle 3001	1	
Bionolle 3001	1.5	Showa High Polymer Co. Ltd Europe [98] Labuzek et al. [117]
PBS	20	SK Chemical Co. (Seoul, South Korea) [101] Kim et al. [90]
Bionolle 1001	1,5	National Sun Yat Sen University [65]
Bionolle 1903	4,5	
Bionolle 1020	25	
Bionolle1020 x30	22	
PBSA 3001	1,4	
PBSA 3020	25	
PBSA 3001	0.8 - 1.8	Showa Highpolymer Co. Ltd [98] Krystyna Twarowska-Schmidt [118]

As shown in Figure 3.3 the melt flow rate (MFR) of PBS is designed by controlling $\overline{\mathrm{M}_\mathrm{n}}$ and $\overline{\mathrm{M}_\mathrm{w}}$ for it to be processed by such methods as those used for polyolefins.

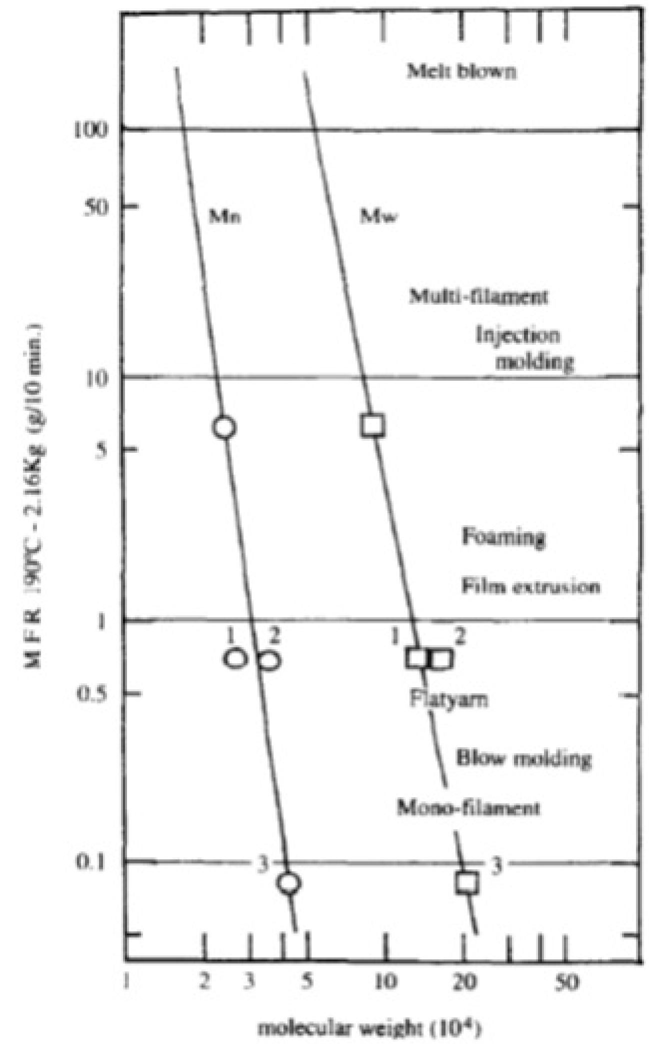


Figure 3.3. Relationship with $\overline{M_w}$, MFR and processing methods [96]

3.3. Thermal properties and transitions

3.3.1. Melting and thermal degradation

The thermal parameters characterizing PBS and its copolymers and also affect the application and processing of the polymer are: glass-transition temperature, melting point, heat distortion temperature, thermal degradation temperature, etc. These thermal parameters can be obtained via differential scanning calorimetry, dynamic mechanical analysis, thermogravimetric analysis, etc.

DSC measures are performed using a DSC analyzer. The DSC scans are recorded under a nitrogen atmosphere in a temperature range 140–150 ^{o}C at a heating rate of 10 ^{o}C /min. The melting temperature is determined from the initial scan as the temperature of the main peak in the DSC curves.

The glass transition temperature is calculated from the DCS scans as the midpoint of the heat capacity change.

The PBS homopolymer has a melting point around 112–116°C, which mainly depends on the molecular weight and the thermal history of the sample preparation. The melting temperature of PBS varies with the thermal history, e.g., the crystallization temperature [10]. Yasuniwa et al. [119] also found that PBS shows two-three melting endotherms upon crystallizing nonisothermally from the melt at a constant cooling rate, which was ascribed to the recrystallization and melting mechanism.

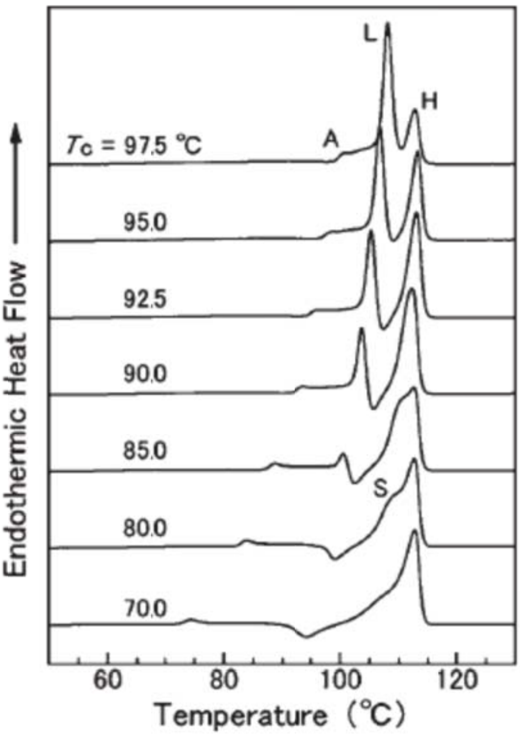


Figure 3.4. DSC curves in the heating process for a PBS resin isothermally crystallized at *T*c's. The heating rate scan was 10K/min. Three melting peaks appear in the DSC curves and are expressed as A, L, and H from a low temperature. In addition, a small peak S appears evidently at the lower temperature of peak H as shown in the DSC curves at Tc = 85 and 80 8^{0}C [119]

Yoo and Im [120] have demonstrated that the middle endotherm corresponds to the original lamellae formed during the previous isothermal crystallization, whereas the highest endotherms peak results from the melting of re-crystallized crystallites during the heating scan.The reorganization of the preformed metastable lamellae leads to lamellar thickening.

Qiu et al. [121] carried out experiments using modulated temperature modulated DSC (TMDSC) in order to give the direct evidences to support the proposed models explaining the melting behaviour of PBS crystallized nonisothermally from the melt. TMDSC is a relatively new thermal analysis technique, which applies a sinusoidal temperature oscillation (modulation) on a linear heating/cooling conventional DSC and makes the total heat flow (such as that from conventional DSC- figure 3.5.) to be separated into the heat capacity-related (reversible) and kinetic (nonreversible) components. Thus, the endothermic signals can be detected in both reversible and nonreversible scans, whereas the crystallization exotherms only contribute to the nonreversible signal. This makes TMDSC (figure 3.6.) a very powerful technique for the separation of exotherms (including crystallization and recrystallization) from glass transitions, reversible melting, or other heat capacity related events. All the results obtained confirmed once more that the double melting behaviour of PBS crystallized nonisothermally from the melt at a constant cooling rate originates in the melting and recrystallization of the crystallites of the low melting endotherm with low thermal stability.

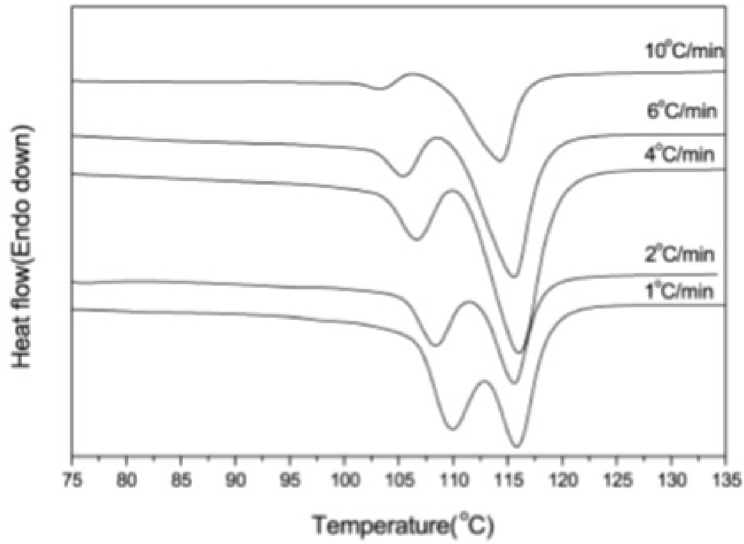


Figure 3.5. Conventional DSC traces of the melting behavior after the nonisothermal crystallization [121]

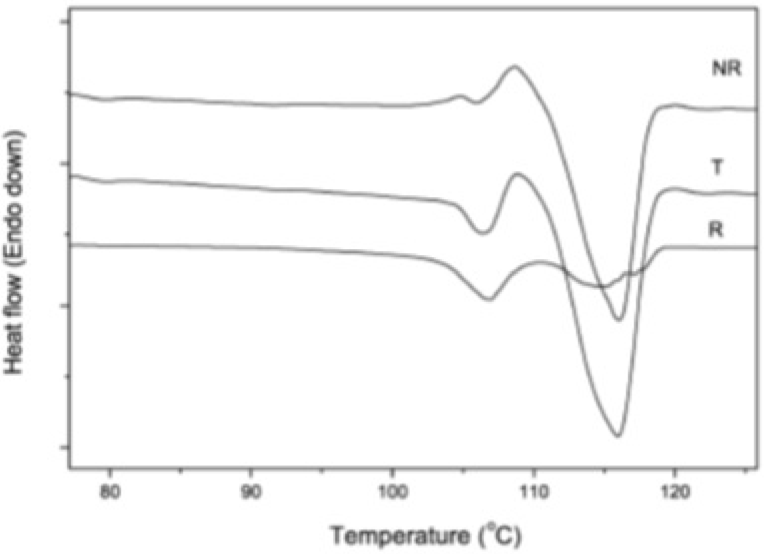


Figure 3.6. TMDSC traces of the melting behavior after the nonisothermal crystallization. In the conventional DSC traces, the cooling rates are shown in the figure; in the TMDSC traces, the three curves from the top to the bottom are nonreversible heat flow (NR), total heat flow (T) and reversible heat flow (R), respectively [121]

In both isothermal and nonisothermlal crystallization, they found that the rate of the recrystallization decreased with the molecular weight. PBS with low molecular weight reorganizes more easily and shows multiple melting peaks over a wider temperature range than that with higher molecular weight.

The thermogravimetric analysis (TGA) of PBS reveals that this polyester shows weight loss of 5, 50, and 90 % at 325, 400, and 424°C, respectively, in air. It should be noted that this does not indicate that PBS polymer chains are thermally stable up to 325°C. On the contrary, PBS shows thermal degradation when extruded at 200°C, which is implied by the decrease of the shear viscosity with prolonged time. The thermal degradation temperatures of PBS are almost the same in nitrogen and air [74].

Concerning the effect of the chosen polymerization catalyst on PBS thermal properties, for Ti, Zr and Sn based catalysts, glass transition temperatures, crystallization temperatures and melting temperatures do not change much. However copolymers synthesized with GeO_2/lactic acid based catalysts are statistical copolyesters with smaller melting temperatures (from 110 ^{o}C to 102 ^{o}C) although the glass transition temperature remains unchanged [94].

The thermal properties of PBS copolymer depend on the copolymer composition. The melting temperature and degree of crystallinity decrease with the increase of the comonomer content when it is more than 30 mol %. When the comonomer content is less than 15 mol%, the copolymers still have a melting temperature higher than 100°C, which is preferred for real applications. This phenomenon is probably due to the fact that the segments of the extender or the other polymer in macromolecular chain act as an impurity, disturbing crystal growth and lowering the regularity of copolymer main chains [71].

The dependence of the glass-transition temperature on the copolymer composition varies with the chemical structure of the comonomer unit. Copolymerization with methyl succinic acid, dimethyl succinic acid, adipic acid, and propanediol results in a decreased glass-transition temperature, whereas copolymerization with benzyl succinic acid and terephthalic acid brings about an increased glass-transition temperature. For example, PBSA copolymers exhibited an intermediate behaviour depending on their composition. The variation in copolymer melting temperature and heat of fusion with composition is shown in Figure 3.6.

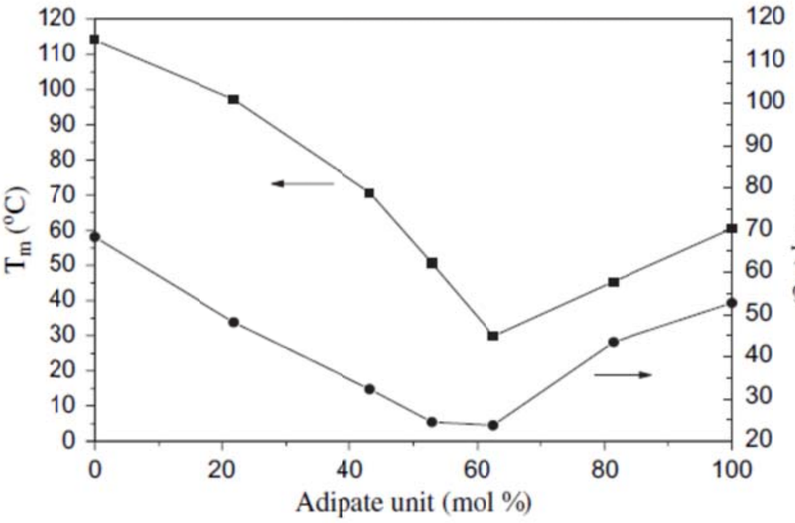


Figure 3.7. Copolyester melting temperature and heat of fusion as a function of composition [53]

3.3.2. Crystallization

PBS is a semicrystalline polyester. Its mechanical properties such as tensile strength, impact strength, and flexibility and its transparency and biodegradability depend on the crystal structures and the degree of crystallinity. Concerning the crystallization behavior of PBS, the thickness of the lamellae mainly depends on the crystallization temperature, and thickening of the lamellae occurs by annealing. When crystallized from quiescent melt, PBS forms spherulites as presented in Figure 3.7.

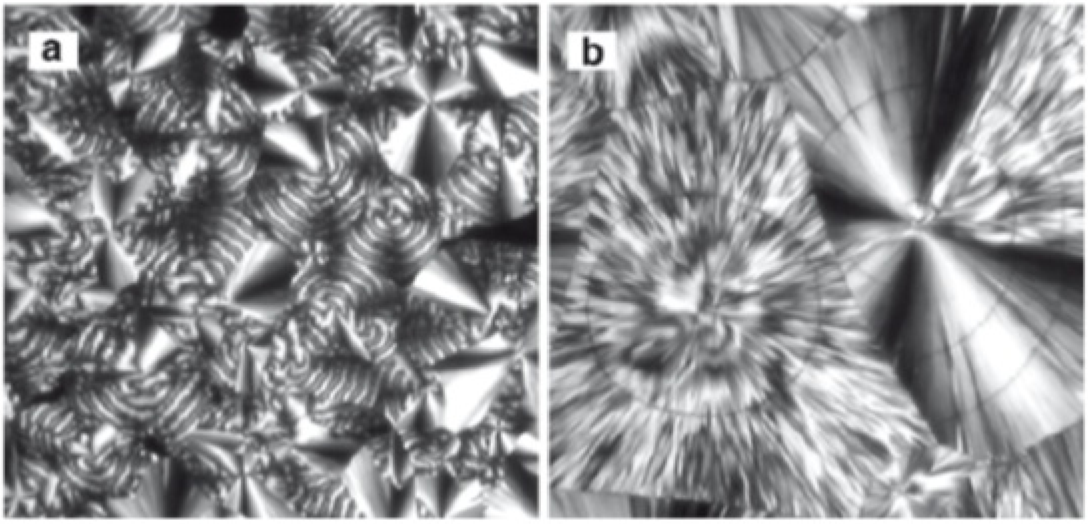


Figure 3.8. PBS crystallized at 70°C (a) and 90°C (b) as observed under the polarized optical microscope [121]

The size and the morphology of the spherulites are affected predominantly by the crystallization temperature. A banded spherulite consisting of circular bright and gray birefringent bands forms over a wide range of temperatures, with further increase of temperature, the regular bands disappear and a coarse-grained morphology prevails. Besides the normal spherulite morphology, some spherulites demonstrate a peculiar winglike region. The results of the atomic force microscope observing PBS film are shown in Figure 3.8.

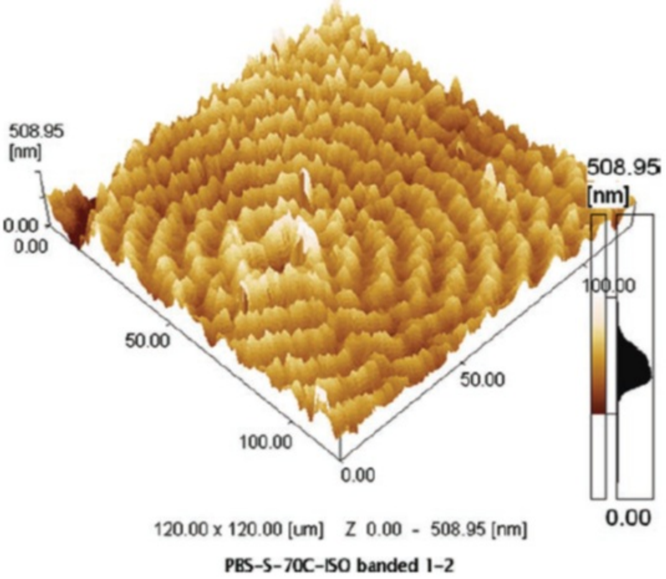


Figure 3.9. Atomic force microscope of PBS banded spherulites [121]

The detailed images obtained from the atomic force microscope reveal that the PBS spherulite consists of radiating lamellar crystals, which splay and branch consecutively during growth, leading to filling of the whole space. This suggests that the cooperative twisting of the lamellar crystals leads to the formation of the banded spherulite.

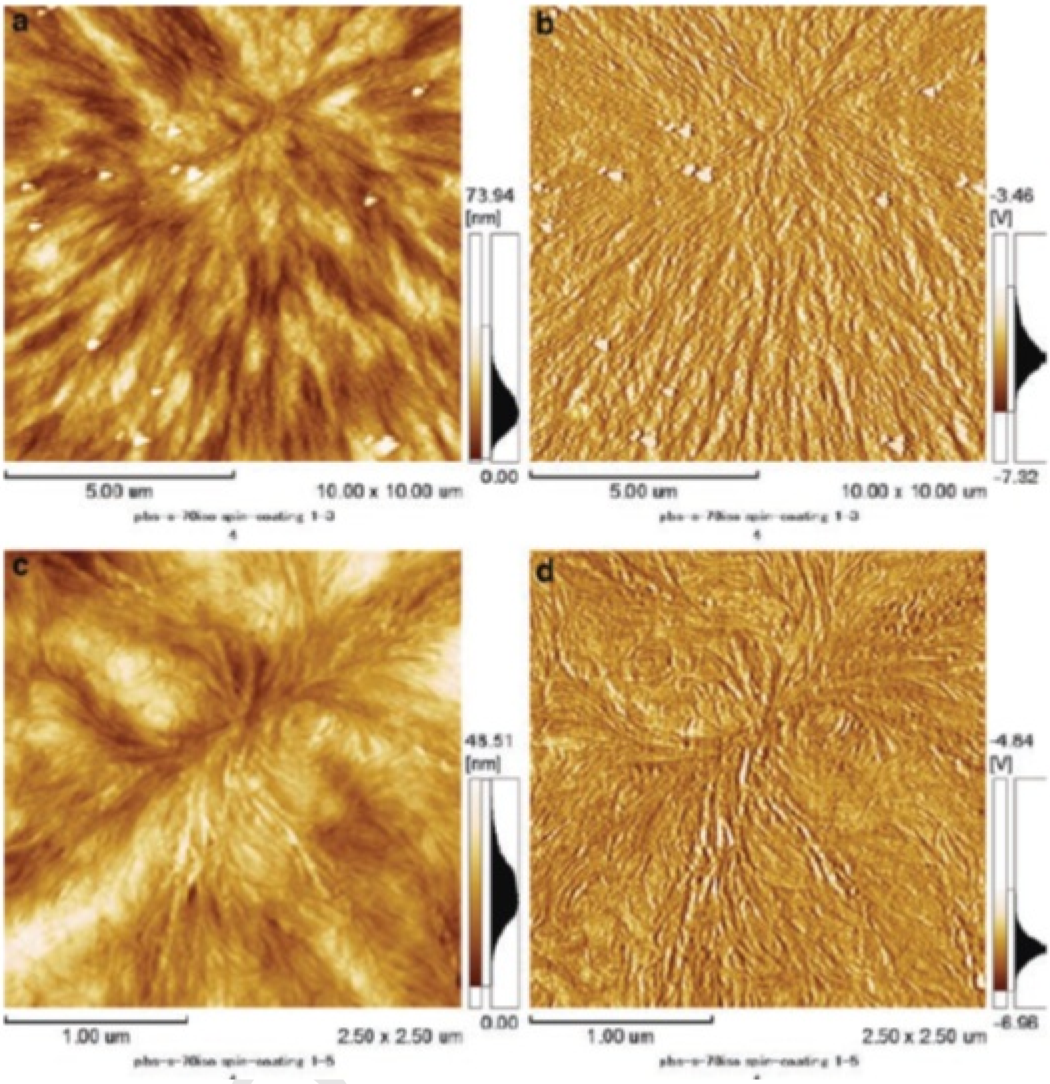


Figure 3.10. AFM images of the lamellae in a PBS baned spherulite [121]

The thickness of PBS lamellar crystals depends on the crystallization temperature. The thickness of the crystalline lamellar core increases steadily and that of the amorphous layer decreases with increase of the crystallization temperature. But the total degree of crystallinity varies little with temperature. This result suggests that the surface of PBS lamellae might consist irregularly of methylene or ester bonds in order to accommodate the chains to smoothly increasing thickness of the lameallae. PBS single crystals grown from solution show terracelike and leaflike shapes depending upon growth temperature. The lamellar thickness increases smoothly with temperature, but not stepwisely, to accommodate the repeating units. This suggests lamellar surfaces composed irregularly of both ester bonds and methylene units [122]. Crystallization temperatures (T_c) range from 70 to 100 °C [120].

The unit cell parameters can be determined from the wide angle X-ray diffraction patterns of the single crystals, films, or fibers. PBS has two crystalline modifications: a and b form, depending on the crystallization conditions. The a form appears when PBS is crystallized from a quiescent melt, whereas the b form occurs under mechanical stress. Both of the modifications belong to the monoclinic system. The unit cell contains two molecular chains; the cell dimensions for the a form are a = 0.523 nm, b = 0.912 nm, c(fiber axis) = 1.090 nm, and b = 123.9° for the a form [122] and a = 0.584 nm, b = 0.832 nm, c(fiber axis) = 1.186 nm, and b = 131.6° for the b form [5] as presented in Table 3.3. too.

Table 3.2. Unit cell parameters of the a and b forms of PBS [55]

Crystalline modifications	**a form**	**b form**
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Cell dimensions		
a (nm)	0,523 (2)	0,584 (5)
b (nm)	0,912 (3)	0,832 (11)
c (nm)	1,090 (5)	1,186 (7)
B (^{o})	123,9 (2)	131,6 (5)
Volume (nm^{-3})	0,4315 (30)	0,4320 (80)
Observed density (g/cm^3)	1,28	-
Calculated density (g/cm^3)	1,33	1,32
Number of chains running through the unit cell	2	2

Using the XRD analysis for the crystalline modifications a and b the results obtained show that the 2θ peak at 19,6°, 21,5°, 22,5°, and 28,8° corresponds to (020), (021), (110), and (111) deflection, respectively [121,123]. Studying the bulk crystallization behavior of PBS films under various thermal conditions with respect to their crystallinity and spherulite morphology. The main characteristic diffraction peaks results were the same (figure 3.11), but they have also mentioned that the isothermally crystallized PBS has the same crystal structure (a-form crystal modification of PBS) even if crystallization temperatures are different.

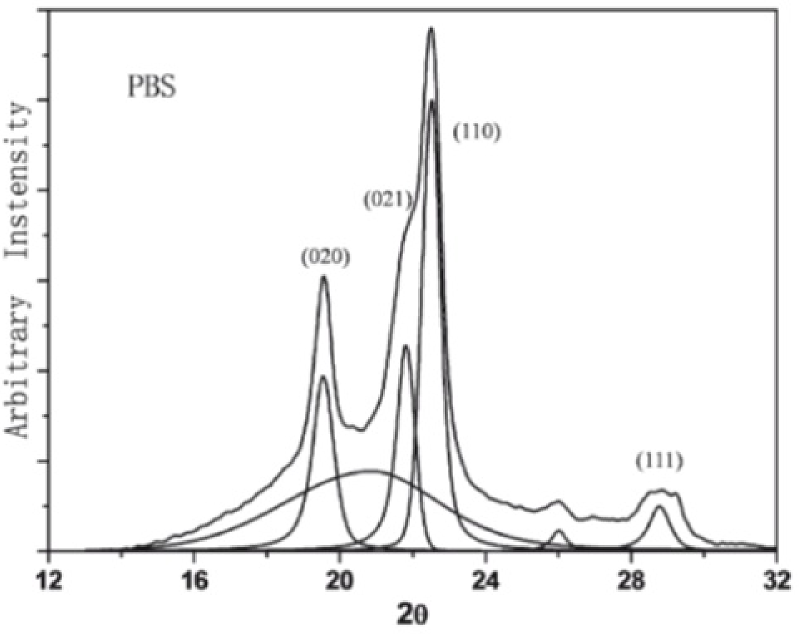


Figure 3.11. Typical X-ray diffraction diagramm of melt –crystallized PBS film

Since the c-axis dimension of PBS is shorter than that of the fully extended chain, the PBS chain includes trans conformations as well as gauche. The molecular conformations of the a and b forms are T_7GT G and T_{10}, respectively, where T, G, and *G* indicate trans, gauche, and gauche minus, respectively. The b form has a more extended chain conformation than the a form. The solidstate transition between the a and b forms is reversible under the application and release of strain [55].

The crystalline structure of PBS copolymers varies with the copolymer composition. The crystallinities of the chain-extended PBS is presented 12.3 % lower than that of PBS prepolymer [56]. Poly(butylene succinate-*co*-butylene terephthalate) (PBST) demonstrates a PBS-type crystalline structure when the content of butylene terephthalate units is less than 30 mol % and shows a poly(butylene terephthalate)- type crystalline structure when the content of butylene terephthalate units is higher than 40 mol%, as demonstrated in Figure 3.12.

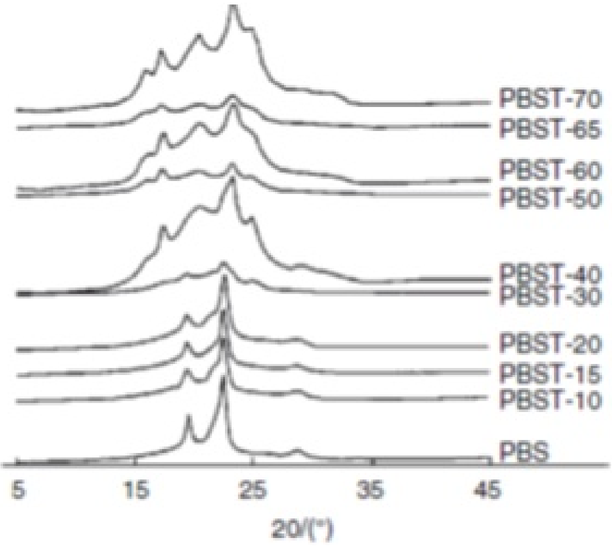


Figure 3.12. WAXD diagramm of PBST [55]

Poly(butylene succinate - co - adipate) (PBSA), exhibits a lower degree of crystallinity than both the respective homopolyesters PBS and PBA. Crystallization temperature (T_c) decreased with increasing branching agent content [124]. However, copolyester PBSA shows the same XRD pattern as PBS, proving that the patterns of copolyesters depend strongly on the composition of the predominant crystal unit [53].

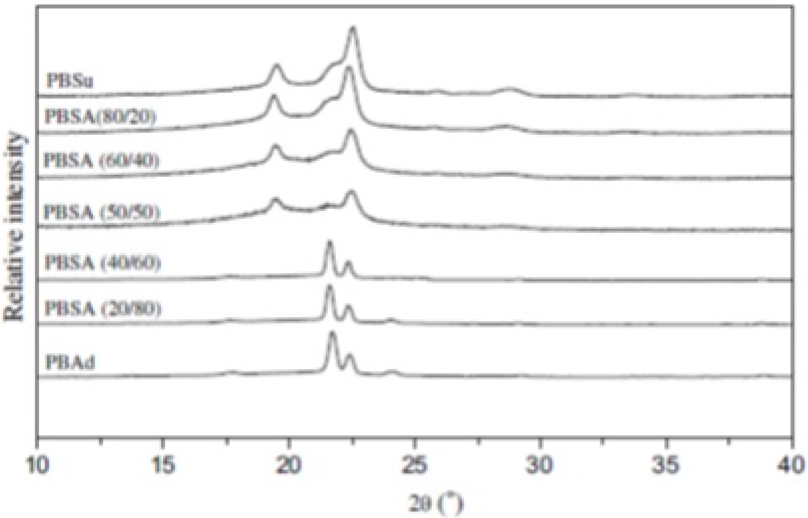


Figure 3.13. WAXD diagramm of PBSA [53]

The characteristic peaks for the copolyester PBSF prove that with increasing unsaturation, the peak positions are shifted to higher 2θ values, which can be assigned to a small decrease of the unit cell dimension. The peak positions in the diffractograms of the copolyesters show that there is no change in the type of the crystal lattice and that the unsaturated copolyesters crystallize in a monocliniccrystal lattice similar to homopolymer [74].

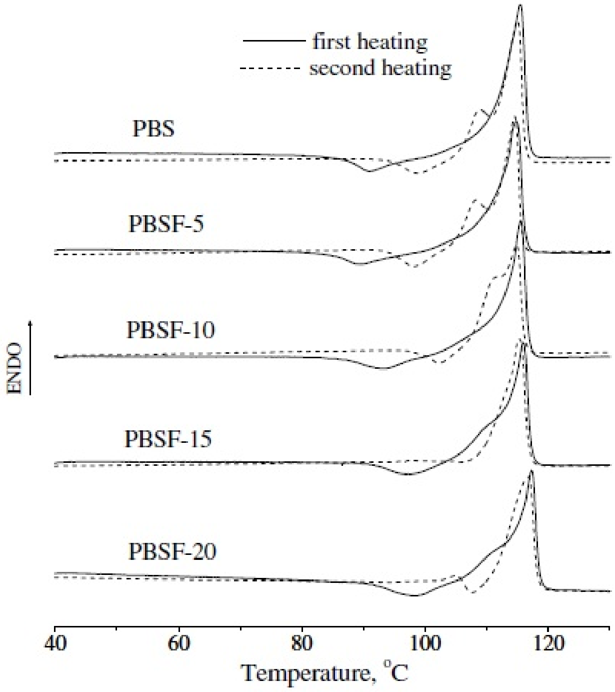


Figure 3.14. DSC diagramm of PBSF [74]

3.4. Mechanical properties

PBS has mechanical properties similar to those of polyolefins such as polyethylene. PBS possesses good tensile strength and impact strength, moderate rigidity, and hardness, and is a typical tough polymer. Physical forces, such as heating/cooling, freezing/thawing, or wetting/drying, can cause mechanical damage such as the cracking of polymeric materials .Properties such as tensile strength are very sensitive to changes in the molar mass of polymers, which is also often taken directly as an indicator of degradation [125].

Comparing PBS with other polyesters such as polyethersulfone, polyphenylene sulfide (PPS), polylactic acid (PLA), PBS is characterized as a hard and tough material. As it can be seen in figure 3.14 the mechanical properties are both temperature and polyester type dependent. An increase in temperature leads to higher tensile strengths. Comparing polyethylene succinate with PBS the former exhibits higher Young’s modulus, although the latter exhibits higher tensile strength especially at high temperatures and higher elongation at break values at all temperatures [93].

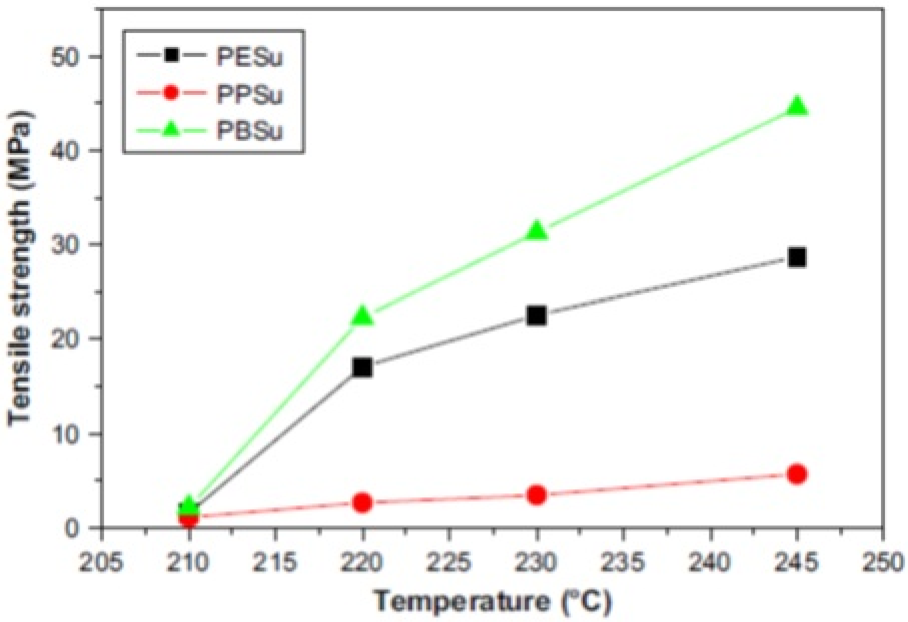


Figure 3.15. Tensile strength depending on temperature for three types of polyesters [93]

The bending strength of PBS if it is immersed in water was investigated and it was found to decrease as the immersion time and the immersion temperature increased due to the chemical degradation of PBS caused by hydrolysis. If it is also reprocessed an unusual increase both in the bending strength and in the molecular weight of PBS take place. To estimate the effects of the material recycling on the mechanical properties of PBS, two major affecters were considered: one is the effect of the number of reprocessing times and the other is the effect of the usage environment. Previous studies revealed that the repetition of processing had a detrimental effect on the strength of the polymer [126].

Copolymerization is a facile method to upgrade the mechanical properties of PBS. The large degrees of chain branches can enhance the horizontal tensile strength and tearing strength of polymer films. Jin et al. [11,123] examined the effect of ethyl and n-octyl branches on the properties of PBS and concluded that the addition of ethyl branches as well as n-octyl branches into PBS improved the biodegradation properties, the elongation at break, and the tear strength without notable decrease of tensile strength and tensile modulus. Wang et al. [84] examined the effect of mol fraction of butanediol segments on the tensile properties of linear PBS. In figure 3.16 (a) it is shown that long chain branched PBS exhibits higher tensile strength than that of linear PBS and increases gradually with increasing the butanediol segments content. In figure 3.16.(b), it can be seen that the elongation at break of long-chain branched PBS is lower than that of linear PBS and decreases gradually as the concentration of butanediol segments increased. The above results showed that the long-chain branches can enhance the tensile strength of linear PBS; however, the elongation at break decreases gradually with the increasing of butanediol segments content.

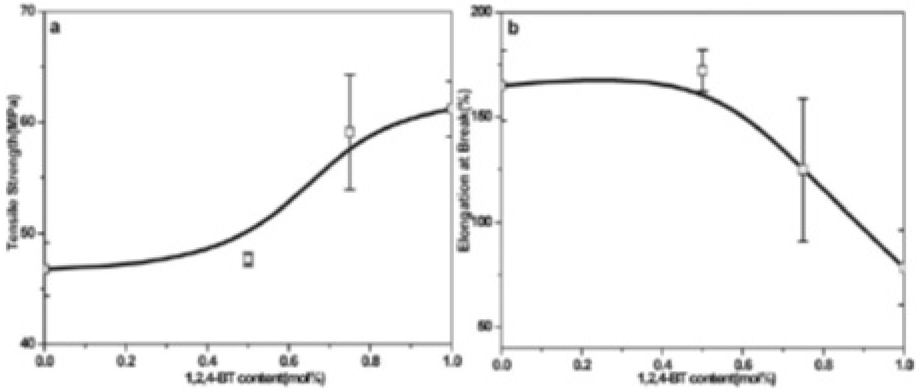


Figure 3.16. Tensile properties of linear and long chain branched PBS with different butanediol content

Concerning fillers, it has to be mentioned that poor compatibility between the filler and the polyester matrix is an issue of concern having a deteriorating influence in the mechanical properties [127]. The most popular additive is starch, which makes such plastic more susceptible to microbial attack however, it may cause poor mechanical properties of composite material. Mechanical properties are dependent on such factors as filler volume, filler particle size and shape, and the degree of adhesion of the filler to the polymeric matrix. Small amounts of starch significantly altered the elongation, however, the negative impact of starch additions on elongation appeared to plateau at the higher starch concentrations [86].

Aromatic monomer groups can also be incorporated into the main chain of aliphatic polyesters for improving their mechanical properties. The introduction of terephthalate units increased the copolyester's mechanical properties but decreased its degradation rate. The homopolymer PBS exhibits the maximum tensile strength 19,3 MPa. PBSA copolymers, which consist mainly of amorphous regions, exhibit quite low mechanical properties as a result of their low crystallinity and molecular weights. Elongation at break increased with increasing adipate unit (20-40 mol %) content, due to the introduction of more flexible groups into copolymer macromolecular structure. However, in the case of equimolarity there was a reduction in copolymer elongation, which could be attributed to the low molecular weight values, observed [53]. Figure 3.17 demonstrates the variation of the mechanical properties of PBST with the copolymer composition.

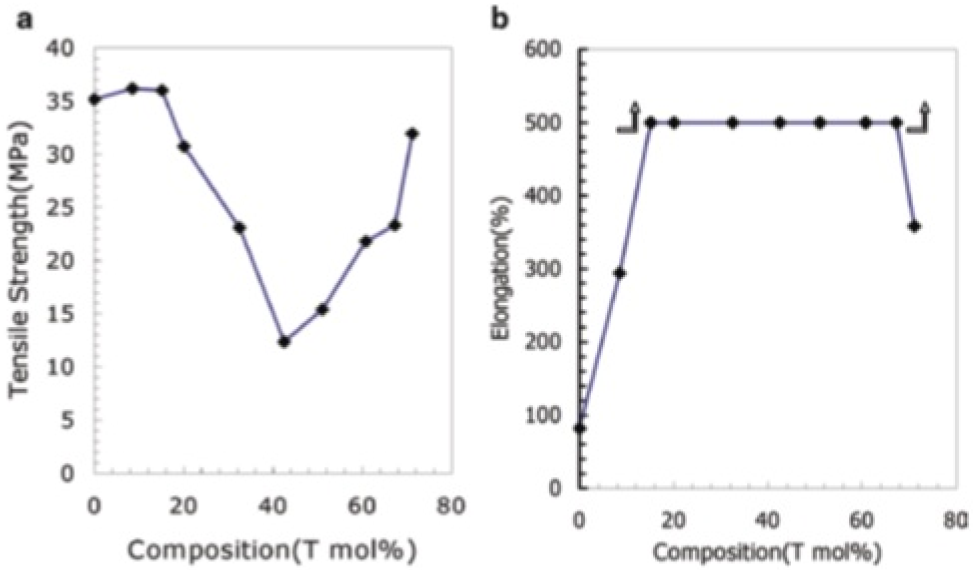


Figure3.17. Mechanical properties of PBST [53]

In the following table typical mechanical properties of PBS are presented.

Table 3.3. Properties of PBS and its grades [128, 69]

Properties	PBS	PBSA	PBSL
Tensile strength	34	19	540
Elongation at break	560	807	94
Izod impact strength	300	>400	-

CHAPTER 4: PROCESSING AND APPLICATIONS OF POLY(BUTYLENE SUCCINATE)

4.1. Modification of poly(butylene succinate): use of additives

Biodegradable polymers derived from renewable resources are attracting lots of interest and publicity, more and more. However lots of studies are required concerning availability, cost, performance, and processability. Bipolymers and among them PBS do need help from additives to address inherent weaknesses in processability, physical properties and prerformance.

Additives can be ranked in three levels. The first one involves traditional additives that have no adverse effect on health or the environment and do not compromise resins' compliance with compostability standards. The second level includes renewable additives derived from natural sources, but not necessarily biodegradable, for use in durable products. Third are additives that are both renewable and biodegradable, which are a good fit for single-use or short-lived products.

Additives can range in a variety of materials from silicon to wood flour, each having its own unique purpose and use [129]. The choice of which additive is needed depends on what is demanded of the end product polymer. Additives are usually combined with polymers in a matrix form, integrating the polymer and additive together. The molecular structure of the polymer is altered so that the additive is incorporated within the very structure of the plastic, altering the properties depending on which additive is included. This allows uniform strengthening of the material as well as replacing some volume that would otherwise be filled with polymer, which can often lead to a less expensive product. When additives are added they must meet standards for compostable plastics such as ASTM D6400 and its European Union counterpart, EN 13432.

4.1.1. Andioxidants and stabilizers in PBS

From packaging to agricultural film, additives that prevent polymer damage from ultraviolet light are becoming more requested. The additive's high opacity reportedly blocks 100 % of UV light, extending product shelf-life while maintaining the gloss of the polymer. The antioxidants and the stabilizers make the polymers resistant to degradation. Poly(ethylene oxide), PEO, is one of these additives. In several studies, it was shown that PBS, modified with PEO presents better biodegradability properties compared to PBS modified with polytetramethylene oxide (PTMO), due to the increased hydrophilicity of the former [130].

4.1.2. Antimicrobial additives in PBS

Antimicrobial properties that can be added to polymers by using additives are of great interest. In medical applications, microbe growth constitutes a threat on multiple surfaces. Additives that can encounter this problem have already been developed. Antimicrobial additives protect polymers durably from microbial infestation, destruction, stains and odors. Except of that additives for controlling bacterial growth also exist. Many of them contain silver, trichlosan, or proprietary agents that kill various microorganisms.

4.1.3 Colorant additives in PBS

Colorants are additives that mainly improve the aesthetic of the biopolymer and improve the characteristics of the final product line, offering denesting, antistatic, slip, antiblock and ultraviolet protection. They are made from nonpolymeric, nonpetroleum-based carrier materials while avoiding reliance on heavy metals or halogens in their formulations. The new colorants can be used in extrusion and blow molding processes.

4.1.4 Biodegradability Accelerants

The biodegradability of PBS and most biopolymers is what makes them more attractive for packaging applications, though they may require some help degrading. Thus, companies have sought ways of making these polymers truly and rapidly biodegradable. For example, there is a compliant masterbatch that is designed to lower the molecular weight of the polymer, speeding oxidative degradation initiated by sunlight, heat, or oxygen. It can be integrated with conventional processes and high-speed molding. The specific masterbatch loading level (typically 1%-4%) dictates the shelf-life of the polymers.

4.1.5 Additives Aid Recycling

Other additives enable the use of more recycled resin in products. Such an additive can give extra clarity and reduce the yellow discoloration associated with recycled resin content. Meanwhile, some companies have already introduced viscosity-modifying additives that aid the incorporation of the recycled polymer.

4.1.6 Flame Retardants

Flame retardants are new and improved tye of additives that do not contain undesirableor dangerous ingredients, such as halogens. Polymers including flame retardants are meant to meet the smoke-density and flame-spread limits of the standard. In figure 4.1. the pyramid of plastics indicates that commodity polymers are the most flammable.

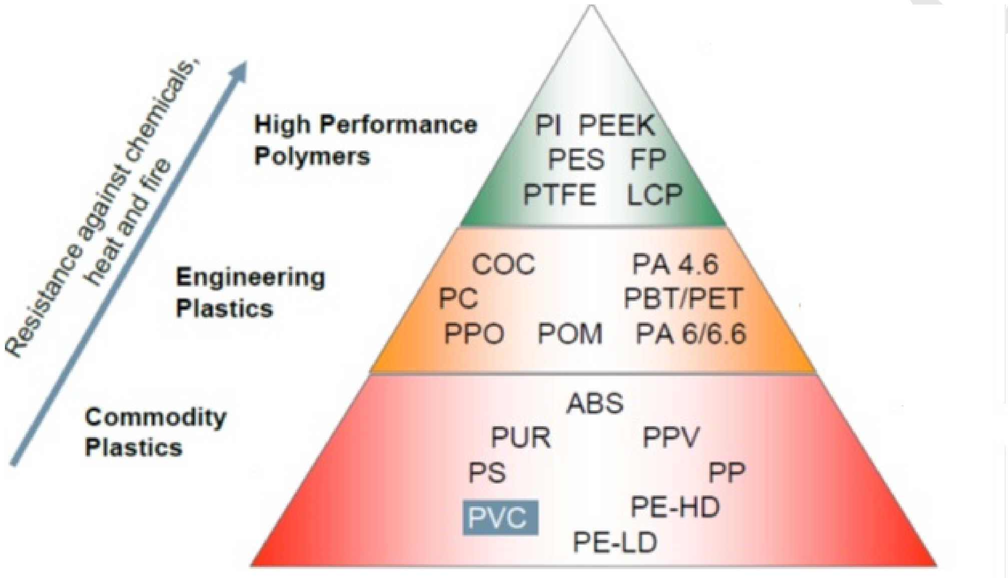


Figure 4.1. Plastics pyramid – Data:Plastics Europe 2008

Measuring the limiting oxygen index (LOI) can identify whether the material is of low or high flammability. A high LOI indicates a lower flammability. According to a recent research by Wang et al. [131] intumescent flame retardant poly(butylene succinate) (IFRPBS) composites with enhanced fire resistance were prepared using graphene as synergist. The limiting oxygen index (LOT) values increased from 23 for the pure PBS to 31 for IFRPBS with 20 wt % IFR loading. The addition of graphene further improved the LOI values of the composites and exhibited excellent antidripping properties. The UL-94 VU materials were obtained with a formulation of 18 wt % IFR and 2 wt % graphene.

The main retardant selection criteria are the following:

- Efficiency/cost
- Ease of compounding
- Adequate thermal stability
- Corrosivity issues
- Physical properties
- Appearance
- Compatibility
- Environment/toxicity

- UV Stability/weathering

Electrical properties

Although effective at reducing flammability, flame-retardant additives and fillers have disadvantages as well. Their poor compatibility, high volatility and other deleterious effects can change properties of polymers. Besides, addition of many fire-retardants produces soot and carbon monoxide during combustion. Halogen-containing materials cause even more concerns on environmental pollution.

4.1.7 Processing Aids

Plastics process aids are indispensible tools for productivity. Fluoropolymer-based melt-processing aids effectively coat and lubricate the walls of process equipment, reducing torque and improving output. Mold release agents can add to the bottom line in injection molding, especially when they can be incorporated into the plastic.

4.1.8 Starch additives

Starch-based polymers have already been presented in Chpater 2, paragraph 2.3.6. as PBS blends. In this parahrpah starch will be described from the point of an additive. Due to the relatively cheap cost of starch additives and its availability, this technique is cost effective and enhances currently used food packaging polymers [132]. Using this additive can provide some biodegradation at a faster rate as well as provides strengthening properties from the starch additive itself. Fang's group [133] showed that increased percentages of starch-based additive, when combined with polymers, showed improved strain curves when force was applied. Though the study focused mostly on film based processing and mechanical function, it did show positive results toward the stability of such polymers. These starch-based polymers can also be thermally processed and can undergo extrusion, injection molding, compression, and film casting [124]. Liu's group showed extensive work on processing techniques that can be used on starch-based materials as well as phase transitions during processing. They also tested processing properties of the starch-based polymers by observing effects of water, glycerol, citric acid and other plasticizers and additives. His group showed that after processing, there was some loss in mechanical function due to temperature changes during processing. The group also showed that processing needed to be controlled and mechanical function of the polymers was based largely on the processing technique and control of moisture within each stage, as an increase in moisture greatly affected the mechanical function in the end stage of processing.

4.1.9 Plasticizer additives for PBS

Cellulose acetate butyrate (CAB) esterified by acetyl and butyryl groups is a brittle and transparent material that it has already been used as a photofilm and a coating material. Some researchers reported that CAB can act as a plasticizer too for some polymers and specially polyesters. CAB is available as a biomass-based plasticizer, and also as an inhibitor for the biodegradation of PBS. Biobased furfural was also listed as a good plasticizer for PBS [134].

4.2. Processing of poly(butylene succinate)

4.2.1. Introduction

Biodegradable polymers can be processed by most conventional plastics processing techniques, with some adjustments of processing conditions and modifications of machinery. PBS has the best processability among the general degradable polymers and it can be processed by injection molding, extrusion molding or blow molding using conventional polyolefin processing equipment, lowering barrier to switch to PBS from other polymers. Depending on the end-use, each PBS grade is processed in a diffent way. Low melt flow rate grades can produce sheet, film and bottles, and high melt flow rate grades can be used for lamination extrusion, injection molding, and fiber extrusion. Grades containing long chain branches show high melt strength and suitable for production of foamed products.

Processability of the polymer depends on thermal stability, viscosity, melt strength and crystallization rate, etc. Thermal stability of PBS materials is sensitive to water content, the content of residual carboxylic acid terminals and the molecular structure of polymer chains.

As already mentioned, according to PBS grade a different process is followed. So, PBS with a $\overline{\mathrm{M_w}}$ less than 100.000 can be used for extrusion and injection molding and PBS with higher $\overline{\mathrm{M_w}}$ or long-chain is more appropriate for film blowing and casting, where high melt strength branches is necessary [96].

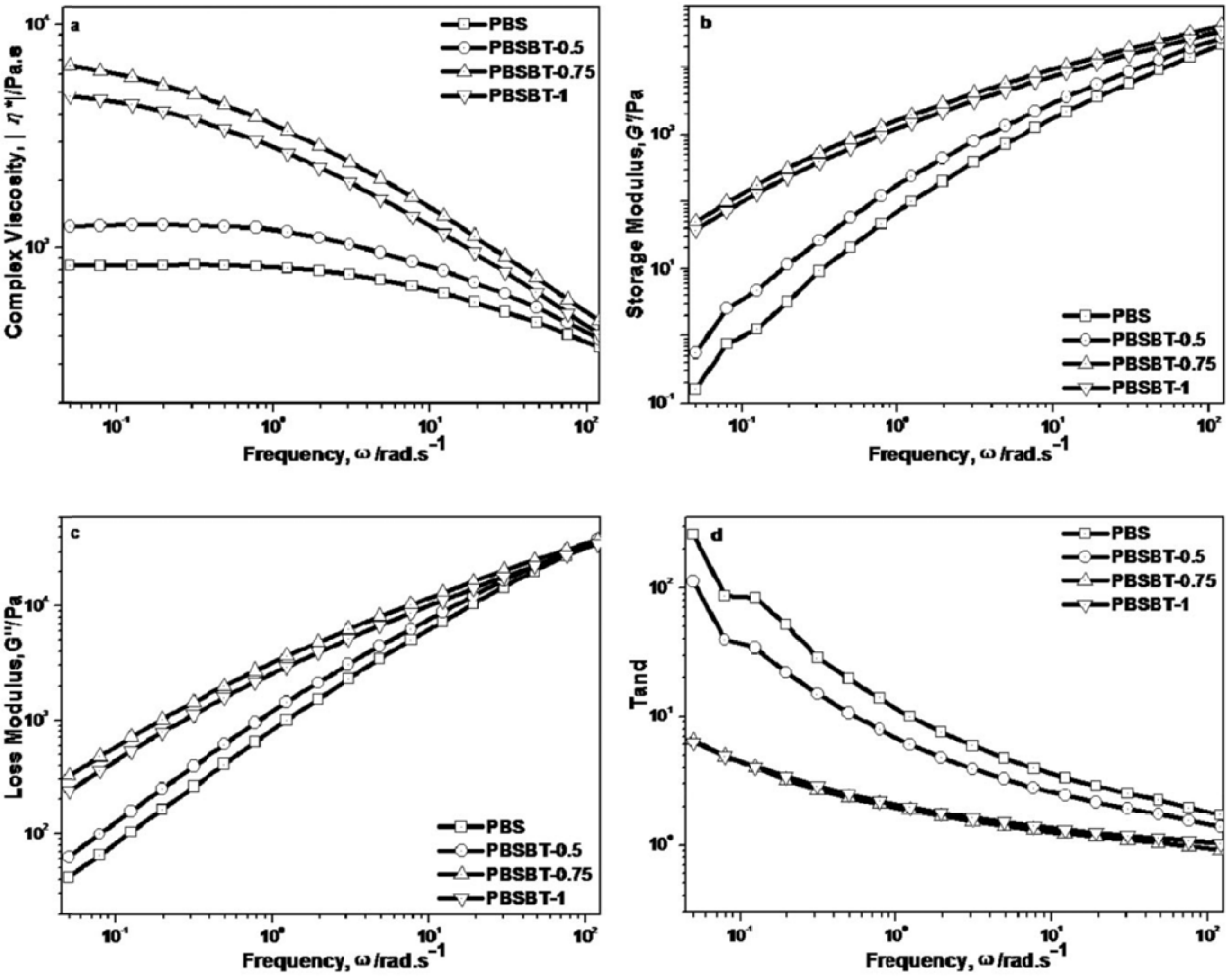


Figure 4.2. Dynamic complex viscosity (|η*|) (a), storage modulus (b), loss modulus (c), and damping factor (d) as a function of frequence of linear PBS and long-chain-branched PBS

In figure 4.2. the rheological behavior of linear PBS and long-chain-branched PBS is presented. It is demonstrated that a small amount of long branches (less than 1%) is able to enhance the zero viscosity, the storage and loss modulus at the terminal region due to more chain entanglements. In addition, entanglements of long-chain branches result in high melt tension, enabling easier production of stretched blown bottles and highly expanded foams [96]. Into fast processing, high crystallization rate is required. In order to manage that, nucleating agents can be incorporated, improving simultaneously the transparency of the end product. Talc and cyclodextrin are two of them. In Table 4.1 processing methods according to polymer grade are gathered.

Table 4.1. Melt flow rate and processing methods for different PBS grades

Grade	T_m (^oC)	Processing methods
PBS (Polybutylene succinate)	110	Injection Molding
PBSA (Polybutylene succinate adipate)	90	Extrusion,Film, Sheet, Extrusion Coating
PBAT (Polybutylene adipate terepthalate)	120	Extrusion, Film, Sheet

In prior to melting processing of PBS, the polymer must be dried sufficiently to prevent excessive hydrolysis (molecular weight drop) which can compromise the physical properties of the polymer. In order to avoid this degradation, the polymer should be sufficiently dried to a moisture level of less than 500 parts per million (ppm) before processing. The drying operation is most efficiently performed by using a commercially available recirculating, dehumidified hot air drying system. A typical drying system is shown in figure 4.3 and the optimum drying conditions in table 4.2.

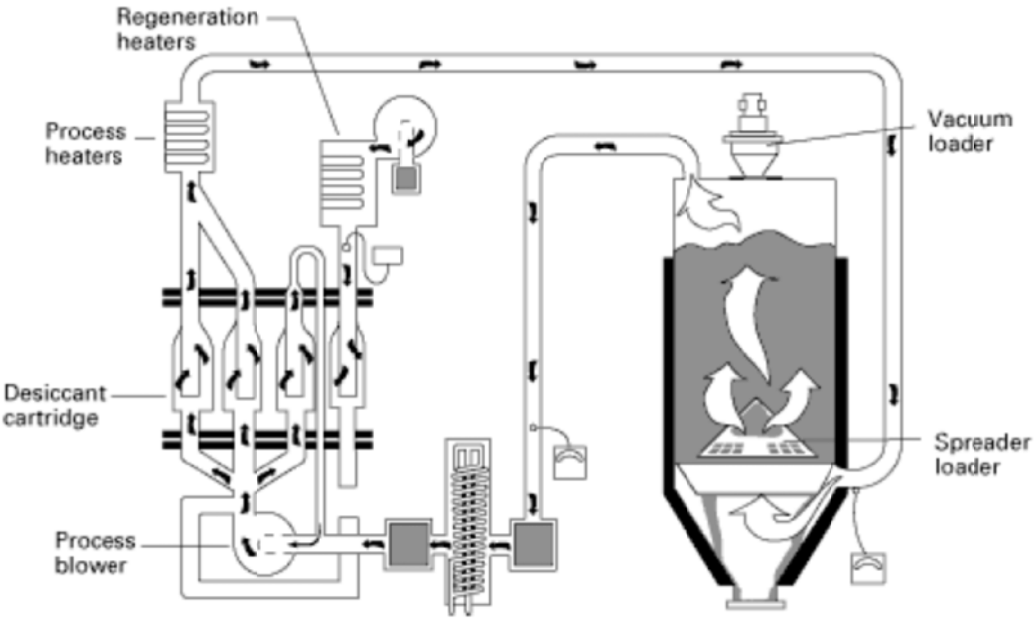


Figure 4.3. Typical drying system

Table 4.2. Optimum drying conditions [135,136]

Drying temperature	65 ^{0}C - 70^{0}C
Drying time	6 -12 h
Air flow of dry air	>0,065 m^{3}/min per kg/h
Dew point of dry air	< -30 ^{0}C
Residual moisture content	<0,05 % (500 ppm)
Drying hopper capacity	6 -12 times extruder output per hour
Height/diameter ratio	>2:1, 3:1 is better for plug flow
Insulation	Insulate well to improve nergy efficiency
Monitoring	Inlet air temperature and dew point

4.2.2. Extrusion

PBS polymer can be processed easier than any other biopolymers and the film produced does not resemble typical biofilms. According to GmbH & Co. KG company, working on PBS cast film processing, the material is supplied in moisture proof bags and provided that it is not exposed to the atmospheric moisture for a long period, no pre-drying is required. Its set point temperature is about 180^{0}C and it is similar to those of many conventional polyolefines. PBS exhibits good draw down from the die lips and the film can be effectively edge-pinned using electrostatics. The film produced at last, has excellent stiffness and mechanical properties and no tendency to yellowing is pbserved. A typical single – screw extruder is shown in figure 4.4.

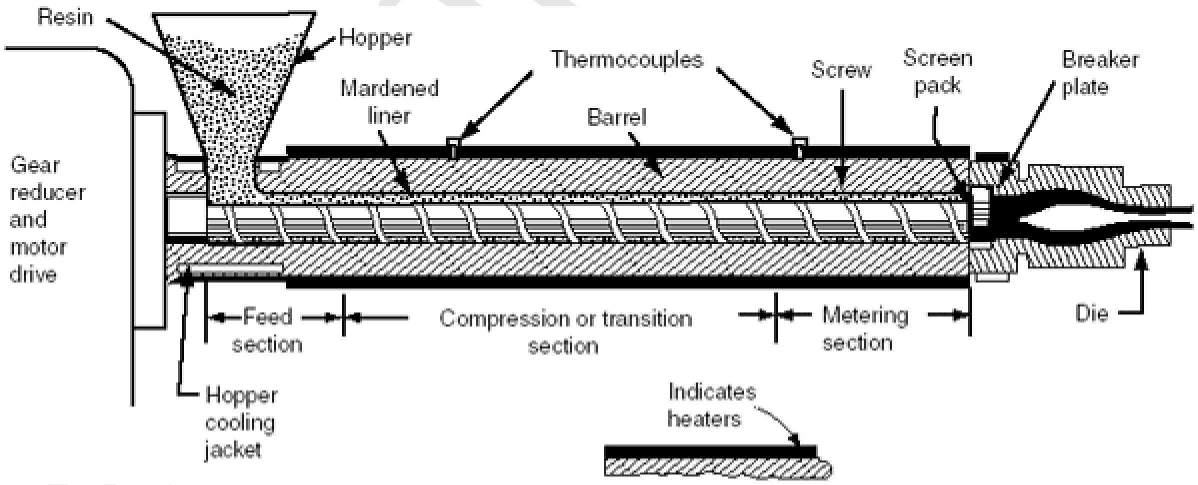


Figure 4.4. Typical single-screw extruder

Ratto et al. [86] produced PBSA with granular corn starch through extrusion blown film processing. All samples were dried at 55^{0}C or 70^{0}C for several hours before processing. The mixed powders then were processed into blown films using a single screw extruder with four heated zones and a blown film die. The film thickness varied from 0,07–0,18 mm. Constant mix times, screw speeds and temperature profiles for the extrusion process were maintained in order to minimize any alternations in the films and any effects from processing parameters. Pivsa et al. [137] with the same method prepared polymer blends of PLA, PBSA and PBAT.This time, the blends were prepared using a twin-screw extruder. Before extrusion, PLA, PBSA and PBAT resin were dried at 80°C for 8 h in an oven in order to remove any trace of moisture to prevent potential hydrolytic degradation during the melt processing. The mixture of PLA/PBSA/PBAT was manually premixed by tumbling in a plastic zip-lock bag, and subsequently fed into the extruder for melt compounding. The extrudate was cooled in a water bath and subsequently granulated by a pelletizer. The polymer sheets (thickness 2 mm) of polymer blends were prepared by compression moulding.

According to SK Chemicals [135] producing SKYGREEN, this material offers the high melt viscosity and non-crystalline properties required for a successful extrusion blow moulding. In the following table all processing data for the production of a 6 mm extruded sheet are presented. Moreover some processing details that should be taken into consideration have to be mentioned:

- If extrusion stopped from more than 15 -20 minutes, the temperature inside should be reduced to about 150°C so as to avoid excessive degradation of the polymer
- When restarting the machine or on initial start-up extrusion should begin as soon as possible after the machine reached the desirable conditions
- On machine shut-down it is recommended that purging materials should not be used

Table 4.3. Processing data for extrusion moulding [135]

Extruder	45 mm single screw , L/D=30/1, 100 rpm, vaccum=40 mbar
Extruder temperature	Zone 1: 180°C Zone 2: 245°C Zone 3: 265°C Zone 4: 260°C Zone 5: 240°C
Melt pressure	83 bar
Die	Zone 1: 247°C Zone 2: 249°C
Roll	1: 45°C 2: 54°C 3: 63°C

Reactive extrusion (REx) is an attractive route for polymer processing in order to carry out melt blending, and various reactions including polymerization, grafting, branching and functionalization as well. It is a special process in which individual components are first bonded by a chemical reaction. Using an extruder for conducting chemical modifications has proven to be an efficient way for low cost production and processing methods, which enhances the commercial viability and cost-competitiveness of the materials. The factor that determines whether the desired objective of the extrusion is met is the screw geometry used in the extruder. The screw geometry controls the residence time, the power input, and the extent of mixing imparted to the melt in the extruder [138]. There are two main challenges in using an extruder for reactive processes: a) reaction time that can be varied from seconds to minutes. However reaction kinetics should be fast enoughto achieve 100% reactant consumption within the extruder and b) undesirable side reactions occurring because of free radicals generated at the beginning of reactions. One of the common undesirable reactions in peroxide initiated processes is the polymer degradation (backbone chain scission) and undesirable intra-polymer cross-linking rather than inter-polymer crosslinking. For this reason process condition should always be optimized [139]. Lindstrom [124] studied reactive extrusion as a tool for synthesizing starch-PBS polymer reactive blends.

4.2.3 Injection molding

Injection molding is one of the most widely used polymer processing method in the plastics industry. It is characterized by low cost, high production rates and dimensional accuracy of the product. Molten polymer is injected into a mold cavity at high speeds and then is allowed to cool and solidify before it is ejected of the part from the mold [140]. A typical injection molding machine is presented in figure 4.5.

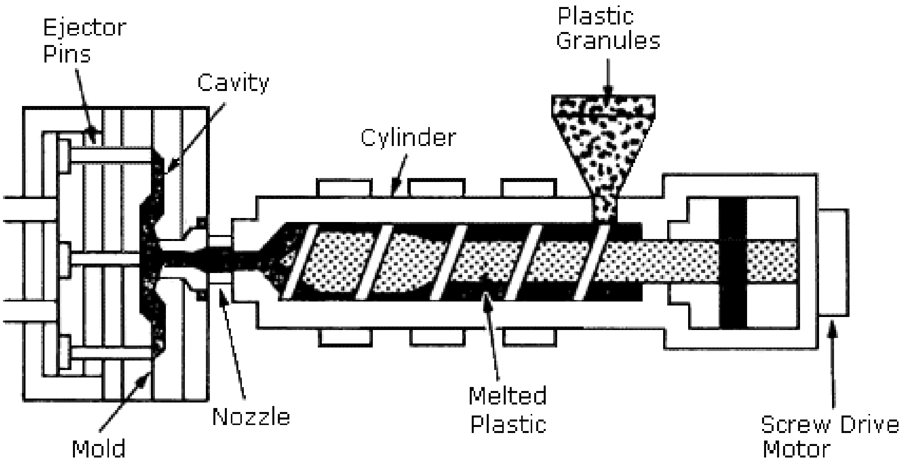


Figure 4.5. Typical injection molding assembly

The preparation of complex injection molded parts sometimes involves the use of multiple gates where polymer melts from different gates meld to form the molded part (weld-line). For example, for the fabrication of short fiber reinforced jute/PBS biodegradable composites, weld-lines are created whenever polymer flow fronts meet, due to the presence of cores, pins or the use of multiple gates. Weld-lines are also formed when jetting occurs along the flow path such as near the gate. The presence of weld-lines significantly reduces the strength of injection molded parts. Injection moulding parameters such as the temperature and viscosity of the molten polymer, mold temperature, moulding clamp/hold/back pressure and mold cooling have been shown to influence weld-line properties. In terms of material parameters, the type and properties of the matrix resin, molded part thickness, the presence of fillers or reinforcing fibers and impact modifiers play a significant role. The combined effects of processing parameters and material properties ultimately determine the ability of the two melt flows to knit together homogeneously [141].

Reviewing Sk Chemicals sheet injection moulding guide for SKYGREEN [136], the main processing data are presented in the table below in relation with general guidlinew fro the process:

- Injection speed: slow to medium and screw speed 50-100 rpm
- Cushion size: minimu (3-13 mm) and decompression is held to minimize drooling
- Back pressure: 0,3 -1MPa is enough to give uniform metering and reduce aire entrapment
- Hold pressure/time: to eliminate sink or voids, but avoid overpacking

Table 4.4. Processing data for injection moulding [136]

Screw type	General purpose, l/D=18/1 to 20/1, compression ration 2,5:1 to 3,5:1					
Temperature (°C)	Mould	Nozzle	C2	C3	C4	Feeding
	40	245	245	245	210	240
Pressure (bar)	1st pressure : 2 2nd pressure: 40,40,35 Back pressure: 5	Speed (mm/sec)			V12 : 8 V21: 8	
Time (sec)	Injection : 2 Hold: 15 Cooling: 15 Cycle: 36	Screw			Refill speed: 50% Rpm: 100 Strike: 62 mm	

Comparing to extrusion molding, injection moulded products are removed from moulds after cooling while extrusion moulded products are typically carried along a conveyor, cooled and cut to the desired length. Moulded products are generally packaged by manual and/or automated means for transportation.

4.2.4 Thermoforming

Thermoforming is commonly used for forming packaging containers that do not have complicated features and generally to shape thermoplastic sheet into discrete parts. The basic principles and key parameters for this processing technology are the following:

- Heat the thermoplastic sheet until it softens
- Force the hot and pliable material against the contours of a mold by using either mechanical, air or vacuum pressure
- Held against mold and allow to cool, and plastics retains its shape
- Speed of vacuum application- vacuum should be applied as quickly as possible
- emperature of the mold- the mold is normally at room temperature, or temperature below solidification point of the plastic
- Size of the bubble
- Plug size

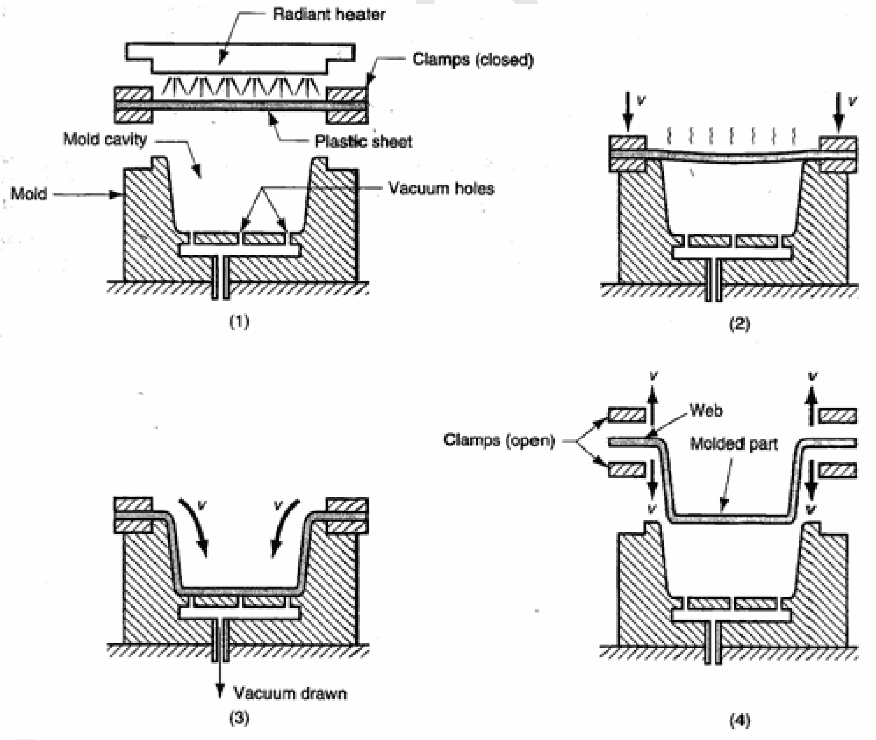


Figure 4.6. Typical vaccum thermoforminh assembly

Thermoforming process is differed from other plastic processing because the material is not melted, lower pressures are required to thermoform (the mold materials is less sturdy materials compared to other processings). The techniques of forming process can be grouped into several types:

- Fundamental Vacuum forming

- Pressure forming
- Plug-assist forming
- Reverse draw forming
- Free forming
- Matched-die forming

The most important sheet property is thickness (variation in thickness over the sheet should be kept under 5%). The uniformity from sheet to sheet is desired, so that the processing parameter can be kept constant, i.e. melt index, if one sheet has a lower melt index than another, the amount of heat to achieve the same formation will be higher than in the sheet with lower melt index. Other variables that might change from sheet to sheet are density, molecular orientation, etc. The advantages and disadvantages of the process are presented in the table following.

Table 4.5. Advantages and disadvantages of the process

Advantages	Disadvantages
Low machine cost	High cost of raw materials (sheets)
Low temperature requirement	High scrap
Low mold cost	Limited part shapes
Low pressure requirement	Oly one side of part defined by mold
Large parts easily formed	Inherent wall thickness variation
Fast old cycles	Internal stresses common

4.3. Application fields of polybutylene succinate

As with conventional plastics, biopolymers have a very broad application spectrum. Poly(butylene succinate) as a polymer being able to decompose naturally into water and CO_2 under specific conditions (contact with soil, light, heat, natural water), has already become of great environmental awareness as a promising alternative to common plastics. Due to its mechanical properties, processability and heat resistance, PBS and its copolymers can be used in a wide range of applications in various industries. So far, PBS has found applications in agriculture, fishery, forestry, civil engineering, packaging and other fields in which recovery and recycling of materials after use is problematic.

According to National Research Center of Engineering Plastic of IPCCAS the characteristics of different industries regarding the application of degradable polymers are set out in Table 4.6 and Table 4.7 depicts the global market of biodegradable polymers in several applications.

Table 4.6. Industries and degradable polymers applications (PBS, PLA, PHB ect.)

Industry	Technical Barrier	Policy Environment	Industry concentration	Necessity for degradable materials	Proportion of cost increment	Applications	Consumer concern
Packaging	Low	Very favourable	Low	High	Higher	Packaging bags, films and bottles	Concern
Agricultural and forestry	High	Normal	Higher	Normal	Higher	Plastic sheeting and pesticide container	Normal
Daily necessity	Low	Normal	Low	Normal	Higher	disposable razors, toys, toothbrushes, diaper pants, bibs, electronics and business equipment	Normal
Medical	High	Favourable	Higher	High	Normal	Medical container and syringe	Concern

Table 4.7. Global market of biodegradable polymers (million lbs) [142]

Application	2006	2007	2012	Compound Annual Growth Rate (%)
Compost bags	173	242	587	19,4
Loose-fill packaging	152	161	214	5,7
Other packaging (includes medical, hygiene products)	51	59	48	23,4
Miscellaneous (unidentified polymers)	33	54	171	25
TOTAL	409	516	1.200	17,3

Showa HighPolymer is the company with on of the biggest production using PBS and its grades in several applications. Agricultural mulch film, foamed cushioning, food packaging and engineering works material, stretched blown bottles and highly expanded foams are some of them. In Table 4.8 the main production of Showa is presented.

Table 4.8. Main applications for PBS and PBSA in global [142]

Sector	% of total production 2003	% of total production in 2020
Packaging (includes compost bag 10% today, 7,5% in 2020)	25	57,5
Building	5	7,5
Agriculture	50	15
Transporation	10	10
Furniture	4	5
Electrical appliances and electronics	2	5
Houseware	4	5
Others	-	-
Total	100	100

4.3.1. Agriculture

For this application, the most important property of biodegradable polymers and specially PBS is in fact their biodegradability. Starch-based polymers are the most used biopolymers in this area. They meet the biodegradability criteria and have a sufficient life time to act.

Plastic films are widely used in agriculture for greenhouse coverings, fumigation and mulching. All principal grades of polymers (plastics, coatings, elastomers, fibres, watersoluble polymers) are utilized in applications which include the controlled release of pesticides and nutrients, soil conditioning, seed coatings, gel plantings and plant protection. As the scope of the application fields is growing, degradable plastics are also of interest as agricultural mulches and agricultural planting containers. Using degradable materials in agriculture is a good way to produce useful soil-improving materials, reducing simyltaneously labour and disposal cost.

Multch films are mainly produced by low density polyethylenes, poly(vinyl chloride), polybutylene or copolymers of ethylene with vinyl acetate. Agricultural mulches help with plant growth and at the end of their life can photodegrade in the fields thereby avoiding the cost of removal. The plastic films are desirable because they conserve moisture, reduce weeds and increase soil temperatures, improving the rate of growth in plants in that way. At the end of the season, the film can be left into the soil, where it is biodegraded. During degradation period, mulches break down into small small brittle pieces which pass through harvesting machinery without difficulty and do not interfere with subsequent planting. Reduced-porosity films can be more effective reducing the escape of volatile chemicals, i.e. nematocides, insecticides, herbicides, etc., and therefore allow for lower application rates.

Figure 4.7. Agricultural mulching films

Another application mentioned before is the controlled release (CR) of biologically active chemicals to a target species at a specified rate and for a predetermined time. The active agent can be dissolved, dispersed or encapsulated by the polymer matrix or coating, or is a part of the macromolecular backbone or pendent side chain. The polymer used in this case serves primarily to control the rate of delivery, mobility, and period of effectiveness of the chemical component. The principal advantage of controlled release application is that less chemicals are used for a specific period so the impact on non target species decreases and leaching, volatilization, and degradation are limited. The macromolecular nature of polymers is the key to limiting chemical losses by these processes [143]. Another application is the bands of sowing, which contain seeds regularly distributed as well as nutriments [144]. In marine agriculture, biopolymers are used to make ropes and fishing nets. They are also used as support for the marine cultures .

4.3.2. Packaging

Most of the packaging that holds the food we consume is neither renewable nor natural. Concerning packaging, it has to be paid attention to the physical characteristics influenced by the chemical structure, molecular weight, crystallinity and processing conditions of the polymers used. The physical characteristics required in packaging depend on what item will be packaged as well as the environment in which the package will be stored. Except of biodegradability, biopolymers have other characteristics too as air permeability, low temperature sealability etc [145]. For example, items which must be kept frozen for a period of time require special packaging and food items there is no doubt that require more stringent packaging requirements than nonperishable goods. The challenge in packaging industry is the development of biodegradable packaging materials either using biodegradable polymers themselves or combining polymers which are truly biodegradable into a laminate film or a film blend which has properties as good as those found in synthetic laminates.

Figure 4.8. Compostable bags

Using PBS, packaging industry is moving a step in the right environmental direction. A PBS application is compostable waste bags in order to collect organic waste and carrier bags, which can also be used as organic waste bags. These bags help reduce landfill by increasing the volume of collected organic waste and moreover improve the composting process and compost quality. Food packaging for snack food sales and film packaging for foods with short shelf life which require attractive presentation, or to extend shelf life. These include compostable pouches, netting and (foam) trays for (organically produced) fruit and vegetables, and recently also fresh meat, plates cutlery and bags. These packagings have the advantage of composition after use along with any remaining food scraps. Spoiled foodstuffs can be recovered via composting with no need for separation of packaging and contents at point of sale.

Figure 4.9. Food packaging and utensils

Moreover, PBS is applied in rigid packaging such as containers and bottles. Bottles made from poly(lactic acid) (PLA) are used for nonsparkling beverages and dairy products. Bhatia et al. [146] have studied the compatibility of biodegrdable PLA and PBS blends for packaging applications. The results of the research showed that both polymers are incompatible beyond 20 wt% of PBS in PLA. However, compositions 90/10, 80/20 (PLA/PBS) seem to be compatible. The shear viscosity of the blend system exhibited shear thinning behavior similar to biodegradable polymers. Blends of up to 20 wt% PBS content in PLA are expected to overcome the deficiencies of polylactic acid such as brittleness, flexural properties, heat distortion temperature and impact strength for applications in food packaging, compost bags, and other biodegradable disposable bags.

Scientists should pay attention when choosing the right material or grade each time in order to avoid migration phenomena of hazardous substances into the food or drinks. A small amount of oligomer remains in PBS and it can possible move to products' surface. For this reason, applications which the plate-out causes problems, purified grades of the polymers are used. By a purification process, the amount of oligomer in purified grades is about one-third of that in general grades.

4.3.3. Medicine

Biopolymers in order to be used in medical applications should abide several conditions. Biodegradabale polymers should have three important properties: biocompatibility, bioabsorbility and mechanical resistance. Current applications include surgical implants in vascular or orthopaedic surgery and plain membranes, but they are also widely used as porous structure in tissue engineering because they typically have good strength and an adjustable degradation speed [147]. Biodegradable polymers are also used as implantable matrices for the controlled release of drugs inside the body. Synthetic polymers are used more widely that others in biomedical implants and devices because they can be fabricated into several differne shapes.

PBS is a promising material concerning bone and cartilage repair [148]. It presents better processability than PLA and it has also higher mechanical properties than PE or PP. For medical instruments and materials PBS it is also used a resin in several blends. The resin may be a PBS copolymer, or a mixture of PBS and a copolymer of PBS with polylactic acid or poly (3-hydroxyalkanoate). However in cases of insufficient biocompatibility it can be enhanced by plasma treatment.

4.3.4. Daily necessity and other fields

Biopolymers are also used in other special applications such as in the automotive, electronics, construction sectors and everyday necessities. In automotive sector, bioplastics and biocomposites aim to prepare lighter cars using natural fibers in plastic car parts . Starch-based polymers can also be used as additive in the manufacturing of tires, reducing as a result the resistance to the movement and the consumption of fuel and in fine greenhouse gas emissions.

As far as construction sector is concerned, inflammability is the main property obtained through biopolymers replacing synthetic fibers. There are also many other applications which do not fit into any of the previous categories concerning every day neccesities.

4.3.5. Potential, near-future applications of PBS

Some grades however present technical problems. Especially, the resin properties have to be improved in order for individual end use applications. For example, in the case of beverage bottles the water and alcohol permeability and gas barrier property of carbon dioxide must be improved, and for applications in horticultural, agricultural and construction fields, the biodegradability in soil must be improved. For diaper application for aged people biodegradable material with super water absorbency and elastic property is needed and must be developed. New grade of PBS will be designed with a break through conception of a new macromolecule structure for various applications such as pressure sensitive adhesives, aqueous emulsions, inks, paints and coatings. Worldwide potential demands for biodegradable polymers will be quite significant, once the technical problems discussed above should be resolved. In the following Table 4.9. a few potential applications of PBS in the near future are presented.

Table 4.9. PBS potential future applications [96]

Processing methods	Potential applications
Injection molding	Cutlery, brush,container
Melt blow	Nonwoven fabric, filters
Multi-filament	Conjugated fiber (core and sheath), knotless net, rascal woven net, nonwoven (planting, diaper, disposable medical supplies, sanitary napkin)
Mono-filament	Fishing line, net, rope
Yarn (flat and split)	Clothand net, planting tape
Film (casting and T die)	Paper lamination, multi-layers
Film (tubular)	Composting bag, shopping bag
Film (oriented)	Shrink film
Flexible packaging	cushion
Sheet extrusion	Food tray, card
Foaming	Soft packaging, cup, vessel
Blow molding (direct)	Shampoo bottle, drug bottle
Bloq molding (injection)	Cosmetic bottle
Blow molding (stretch)	Beverage bottle

CHAPTER 5: DEGRADATION AND RECYCLING OF POLY(BUTYLENE SUCCINATE)

5.1. Degradability of PBS

Degradable plastics including PBS and its copolymers can decompose to the environment, degrade into CO_2 and water, through naturally occurring degrading enzymes and microorganisms. Consequently, these biodegradable plastics will find wider and wider applications as disposable film or articles. PBS can be degraded through hydrolytic degradation, enzymatic degradation, and biodegradation in environmental conditions, such as burial, activated sludge, and compost. The biodegradation rate of PBS and its copolymers depends on several parameters such as: chemical structure, crystallinity, macroscopic shape of the articles and degradation conditions.

5.1.1. Non enzymatic hydrolytic degradation of PBS

Hydrolytic degradation of PBS and PBSA was carried out over a temperature range of 180–300°C for periods of up to 30 min. The hydrolytic degradation temperature was set to be much higher than the T_m of PBS (114 ^oC) and PBSA (94 ^oC) to melt the polymers completely and, therefore, to elevate their hydrolytic degradation rate. Succinic acid and adipic acid at degradation temperatures of 250–300 ^oC were recovered at maximum yields of 65–80 %, whereas butanediol was recovered at a maximum yield of only 30 %, probably because of its decomposition, although the TOC values reached about 90 % of the theoretical values. Such low monomer yields or differences between TOC and monomer yields are probably a result of the decomposition of the formed monomers [149]. The higher hydrolytic degradation rate of PBS comparing to that of PBSA copolymers degradation rate is shown in Figure 5.1

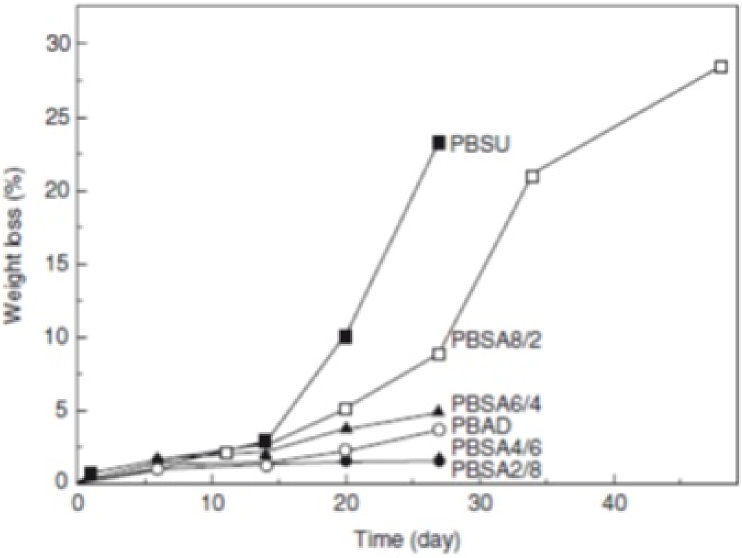


Figure 5.1 PBS and PBSA degradation rate at 30ºC [150]

pH has a considerable effect on the rate of hydrolytic degradation. At pH 13, PBS can lose 3–8 % of its weight after degradation for 9 days. At pH 10.6, the weight loss of PBS can reach 23 % after hydrolytic degradation for 27 days. At pH 7.2, the weight loss is less than 10% after 9 weeks, but in the following period, the degradation accelerates greatly. More specifically PBS loses 75 % of its weight after 15 weeks, as shown in Figure 5.2 [151].

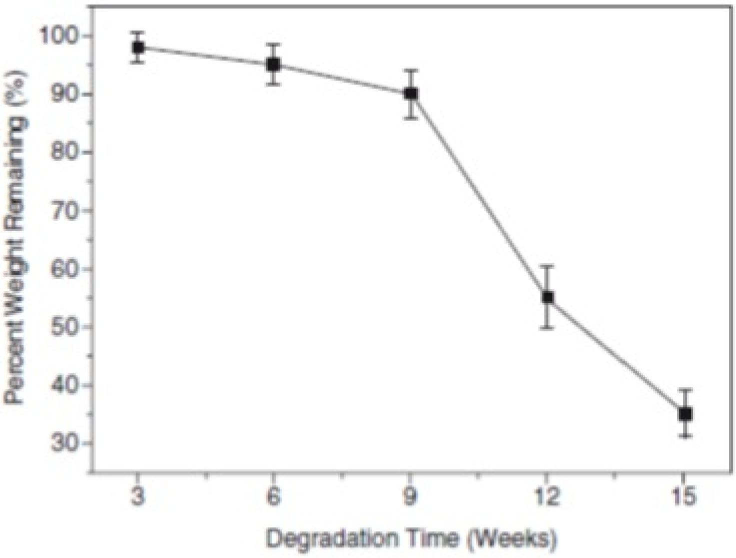


Figure 5.2 Weight remaining (%) compared with day 0 values Degradation in phosphate buffered solution [151]

A traditional way to follow hydrolytic degradation is to measure the weight loss. There is a significant difference in the hydrolysis rate depending on the degradation media. PBS aged in water showed up to 8 % higher weight loss than PBS aged in phosphate buffer. In the hydrolytic degradation, the molecular weight decreases steadily with time, which indicates that hydrolytic degradation proceeds via random chain scission, as revealed in Figure 5.3

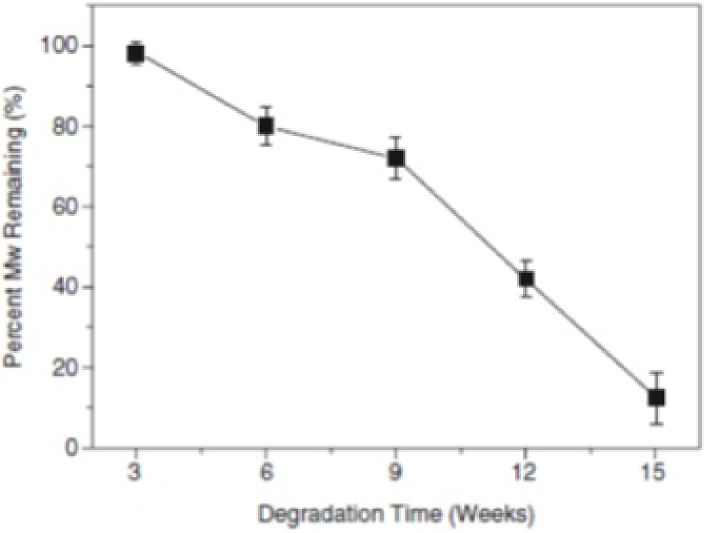


Figure 5.3 Mw (%) remaining compared with day 0 values – Degradation in phosphate buffered solution [151]

Hydrolytic degradation of PBS is also affected by polymer's morphology, which controls the diffusion of water into the polymer matrix. Water penetrates at a higher rate in the amorphous region than in the crystalline region, which results in a higher hydrolysis rate in the amorphous region. The higher degradation rate in the amorphous region is attributed to the easier diffusion of water molecules into the interior of polymers. The central part of the spherulites and spherulitic impinging lines is degraded first, followed by the other parts of the spherulites. Moreover, the internal structure of the spherulite also played an important role in hydrolytic degradation.

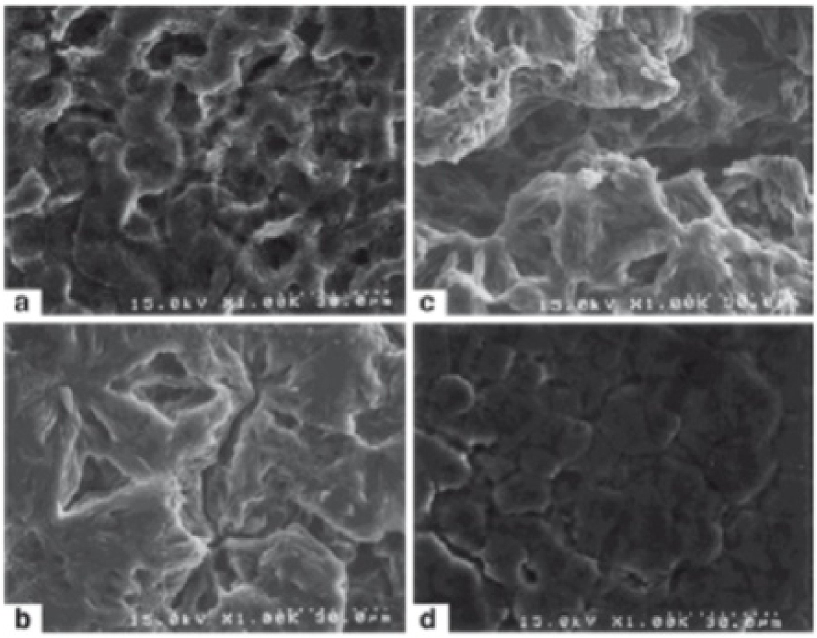


Figure 5.4. SEM pictures of degraded PBS crystallized at different temperatures after hydrolysis for 9 days a) melt quenched b) isothermally crystallized 25°C c) isothermally crystallized 60°C d) melt quenched and annealed at 75°C [108]

One of the most important parameters that affects hydrolysis rate is aging temperature. During aging at 37°C the amount of succinic acid and 1,4-butanediol increased slowly as a function of hydrolysis time. The amount of 1,4-butanediol detected was slightly higher than the amount of succinic acid and this is probably because of the excess of 1,4- butanediol used during the synthesis of PBS. As expected there was a large increase in hydrolysis rate and amount of monomers formed when the aging temperature was raised from 37°C to 70°C. The excess of butanediol over succinic acid was also seen during the first weeks at 70 °C. However, after 3-4 weeks the hydrolysis rate accelerated significantly and the amount of monomers increased rapidly between 4 and 12 weeks [108]. Figure 5.5 shows the degradation profile of PBS samples crystallized at different temperatures. PBS isothermally crystallized at 60°C underwent the fastest hydrolytic degradation, whereas that quenched and then annealed at 70°C demonstrated the lowest degradation rate, indicating the importance of crystallinity.

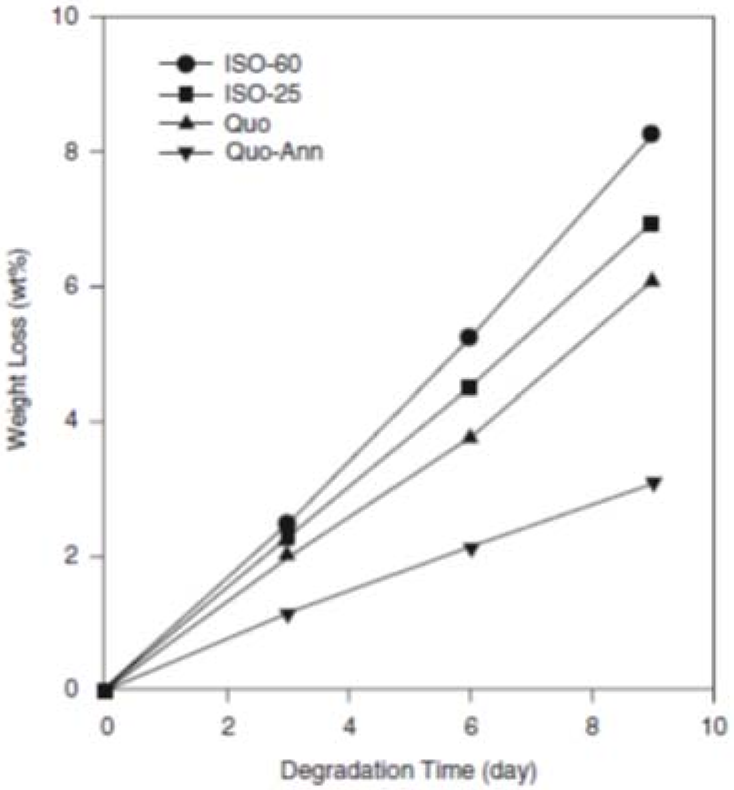


Figure 5.5. Weight loss of PBS crystallized at different temperatures [108]

Hydrolytic degradation is also a potential method for monomer recovery of PBS after its use, belonging to chemical recycling approach (as it will be presented in paragraph 5.2.2). To overcome the very slow rate of hydrolytic degradation in the solid state, owing to the highly hydrolysis resistant crystalline residues (or extended chain crystallites), hydrolytic degradation in the melt has been developed without the aid of a catalyst [149].

5.1.2. Enzymatic hydrolytic degradation of PBS

After several studies it has been shown that PBS, and its copolymers are enzymatically degraded by lipases such as *Rhizopus delemar, Rhizopus arrhizus, Mucor miehei, Pseudomonas sp , Aspergillus niger, Chromobacterium viscosum, Rhizopus orizae, and Rhizopus niveus*. The enzymatic degradation of aliphatic polyesters depends on the chemical structure and the highly ordered structure as regards its specific solid-state morphology and degree of crystallinity [152].

Crystallinity has been singled out as the factor that affects mostly enzymatic degradation of polymers. It is long known that the degradation of aliphatic co-polyesters is faster with respect to the single homopolyesters. The melting temperatureof polyesters has also a strong effect on the enzymatic degradation of polymers. The higher the T_m, the lower the biodegradation of the polymer [153].

Taniguchi et al. [69] examined enzymatic hydrolysis of PBS and poly(butylene succinate-co-L-lactate) (PBSL) with lipase originated from *Pseudomonascepacia*. It has been found that the drawn fibers of PBSL are readily hydrolyzed by the action of the lipase, comparing to those of PBS undergo little enzymatic hydrolysis. Since the polymer films of PBS and PBSL are readily hydrolyzed under the same conditions, the enzymatic hydrolysis should depend not only on the crystallinity but also on the molecular orientation. However, PBS fiber has a much lower degradation rate than PBS film. PBS fiber and film showed weight losses about 6 and 76 % after being incubated with Lipase PS® at 50°C and pH 6.0 for 2 weeks as it is shown in figure 5.6.

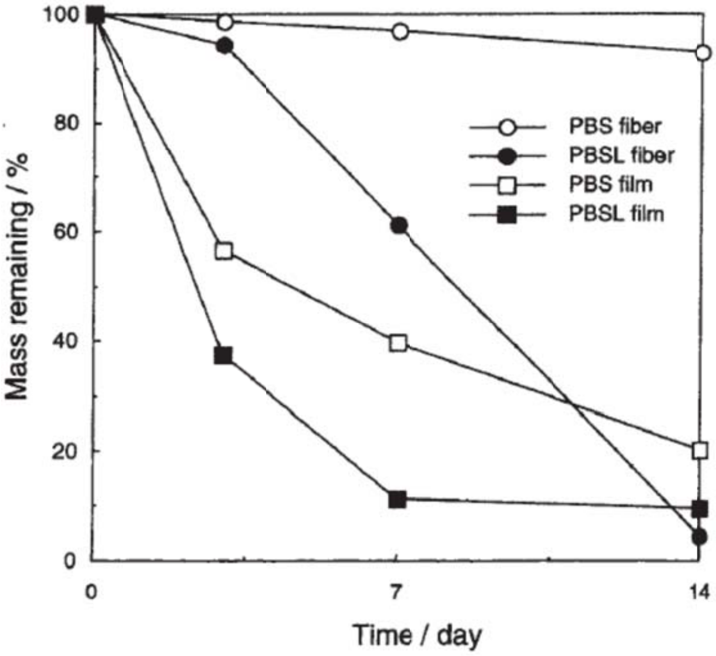


Figure 5.6. Mass remaining of various PBS and PBSL samples as a function of time. The samples were incubated with Lipase PS1 at 50 8C and pH 6.0 [69]

Concerning aliphatic–aromatic PBS copolymers, the enzymatic biodegradation rate decreases with increasing aromatic comonomer content [78, 154]. For PBSA copolymers, those with the lowest degree of crystallinity demonstrate the highest degradation rate in lipase solution [60, 77].

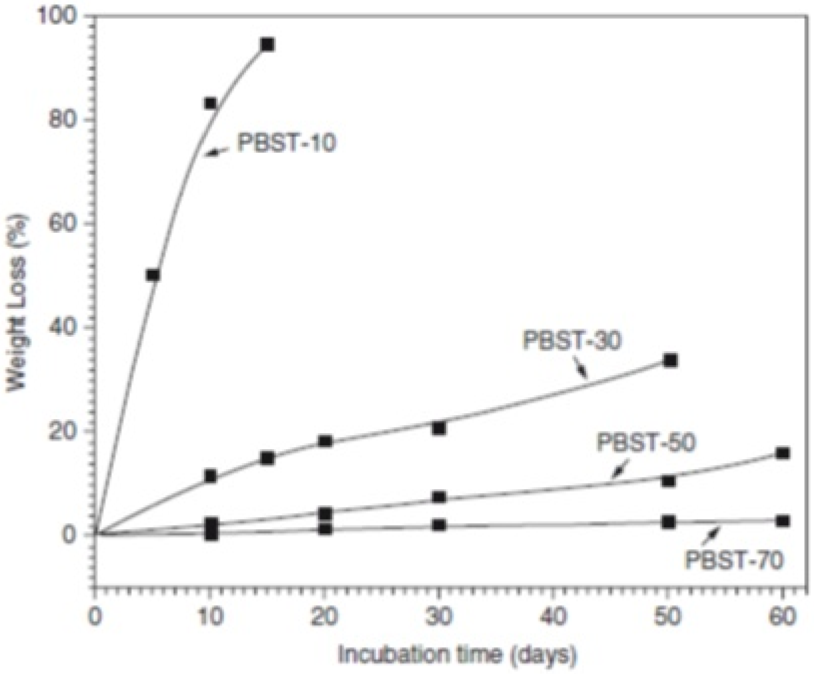


Figure 5.7. PBST weight loss degraded by lipase from Pseudomonas [151]

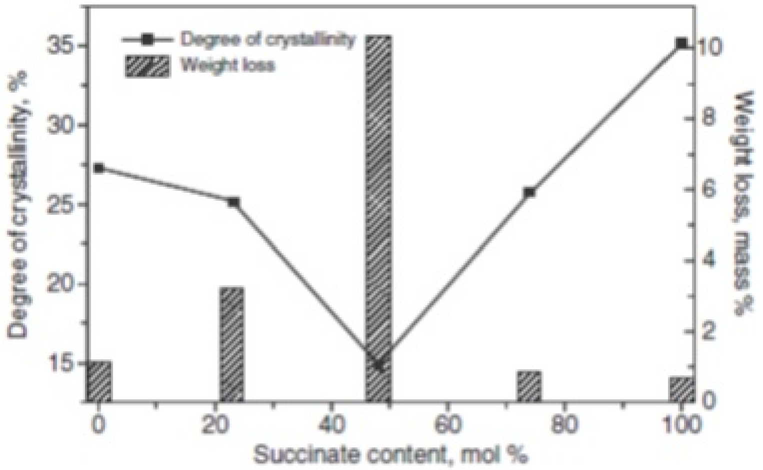


Figure 5.8. PBSA weight loss degraded by lipase from candida cylinracea [77]

It is known that polymer degradation usually proceeds in a selective manner, with the amorphous regions being preferentially degraded as compared to crystalline ones. Both surface erosion and the weight loss, take place. The molecular weight and molecular weight distribution do not change during the enzymatic degradation because only the polymer on the surface of the substrate is degraded and the low molecular weight degradation products are removed from the substrate by solubilization in the surrounding aqueous medium.

The enzymatic degradation is not affected by the molecular weight of aliphatic polyesters and the degradation trends for low molecular weight ($\overline{M_w}$: 6300) and high molecular weight ($\overline{M_w}$: 29,000) poly(butylene succinate) are similar. The lack of any dependence of the enzymatic degradation on molecular weight would indicate that the lipases produced by microorganisms are endo-type enzymes. That means that these enzymes randomly split bonds in the polymer chains. Thus, the variations in the rate of enzymatic degradation are not attributable to molecular weight differences in the series of synthesized polyesters but to their chemical structure [155].

5.1.3. Environmental biodegradation of poly(butylene succinate)

PBS and its copolymers can be degraded in compost, moist soil, natural water, activated sludge and sea water. In the following table the relation between Bionolle grades (PBS, PBSA) and biodegradability is presented.

Table5.1. Polymer structure and biodegradability in different environments [96]

Degradation environments	PBS	PBSA
Hot compost	normal	Rapid
Moist soil	Normal	Rapid
Sea water	Slow s	Rapid
Water with activated sludge	slow	Slow

Degradation in soil is also affected by the same parameters as enzymatic hydrolysis, although there is a difference in their degradation mechanism, since in the case of soil burial the effect of microorganisms arises on the surface of the polymer. Microorganisms in the soil extract liquid can degrade PBS and the pH of the degradation liquid does not change significantly.

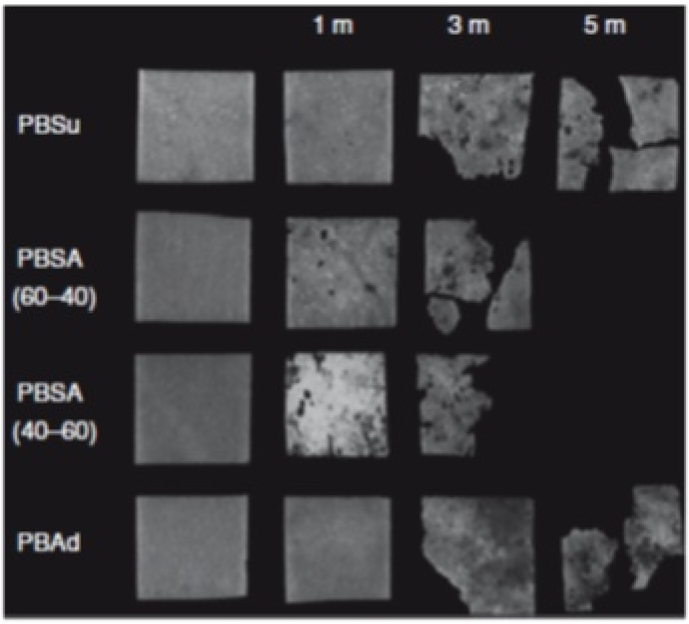


Figure5.9. SEM micrographs of PBS homopolymer and PBSA copolyesters after soil burial [53]

The percentages of degrading bacteria for PBS in the soil environment have been estimated to be 0,2–6,0 % of the total colonies with Bacteria phylogenetically related to the genus *Roseateles* showing the highest degrading activity of all examined [156]. The biodegradability of PBS copolymers also depends on the copolymer composition and the content of the aromatic comonomers [157]. For the aliphatic copolyesters, the greatest biodegradability occurs at about 30–50 mol% comonomer content.

Kasuya et al. [158] studied PBS degradation in different environmental natural waters. Results showed that the rate of biodegradation of chemosynthetic polyesters is dependent not only on the chemical structure of monomeric units but also on the source of natural water used. More specifically, the rate of biodegradation decreased in the following order: seawater from the bay> freshwater from the river > freshwater from the lake > seawater from the Pacific Ocean.

Biodegradation of PBS and its copolymers in activated sludge is faster than in soil burial. For PBS film, a considerable change in the film morphology could be observed after it had been immersed in activated sludge for 2 weeks. After 10 weeks of biodegradation, big holes were observed in the PBS film, as shown in Figure 5.10.

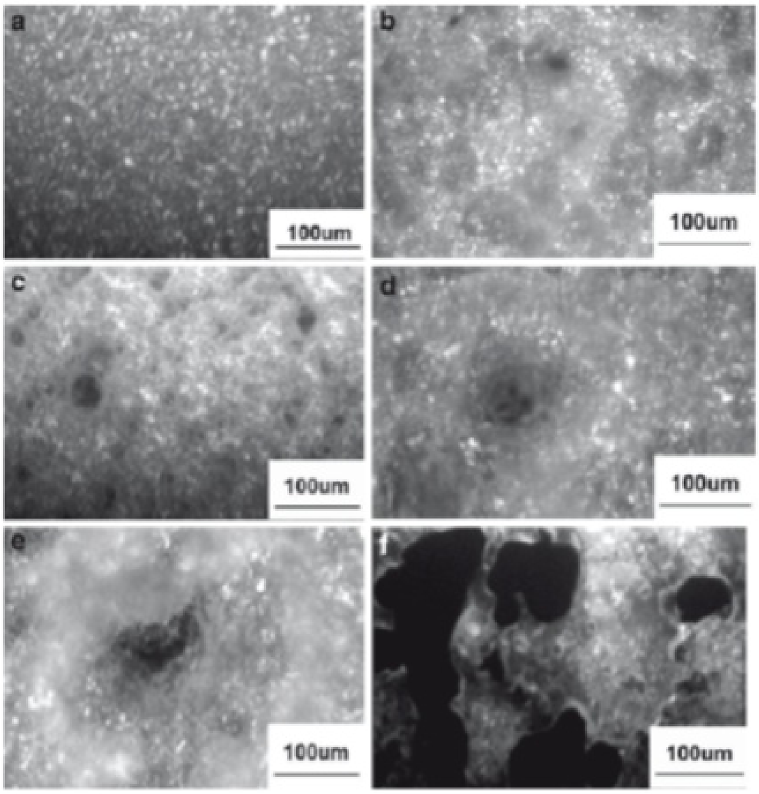


Figure 5.10. PBS degradation in activated sludge a)before degradation b) 1 week c) 2 weeks d) 4 weeks e) 6 weeks f)10 weeks [55]

The molecular weight has a considerable effect on biodegradation of PBS in activated sludge. After biodegradation for 12 weeks, PBS with intrinsic viscosity 1,049 dl/ g has a weight loss of about 80 %, which is much larger than the weight loss of PBS with an intrinsic viscosity of 1,79 dl/ g, about 16 %.

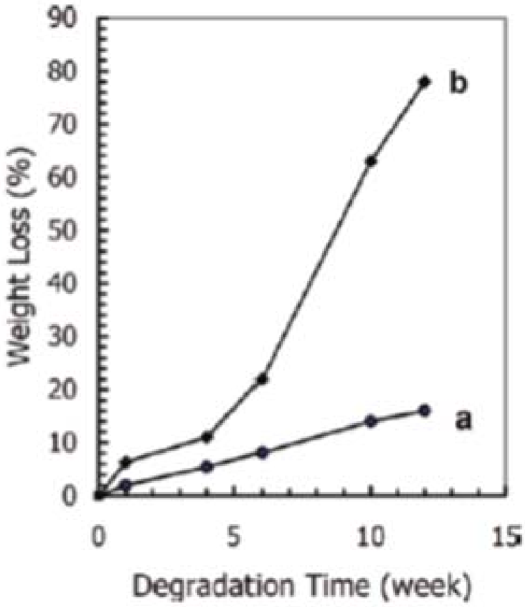


Figure 5.11. Biodegradation of PBS in activated sludge with viscosity a) 1,793 dl/ g b) 1.049 dl/g [55]

Concerning PBS copolymers, the biodegradation rate depends on their chemical structure. For PBSA copolymers, the biodegradation rate in activated sludge improves with increase of the butylene adipate content from 0 to 20 mol %. For PBS copolymers with substituted succinic acid as the comonomer, at the same comonomer content of 10 and 20 mol %, the degradation rate follows the order PBSM > PBSA > PBSBS > PBS. For PBST copolymer, with increase of butylene terephthalate comonomers, the biodegradability increases first, and then decreases sharply. It is observed that the aromatic units are not so susceptible to biodegradation as the aliphatic units.

Biodegradation in compost is the best way to examine whether a plastic is biodegradable or compostable. PBS powder shows a degradation rate comparable to that of the film. PBS pellet degrades more slowly and shows a final weight loss of less than 15 % after degradation in compost for 3 months. The biodegradation rate of PBS in compost depends on the shape and the size of the specimen [159,160]. PBSA powder has biodegradation rate similar to that of the film [159]. PBSA has a higher biodegradation rate than PBS. The weight loss of PBSA and PBS is around 90 and 55 % after degradation in 60°C compost for 3 months [160].

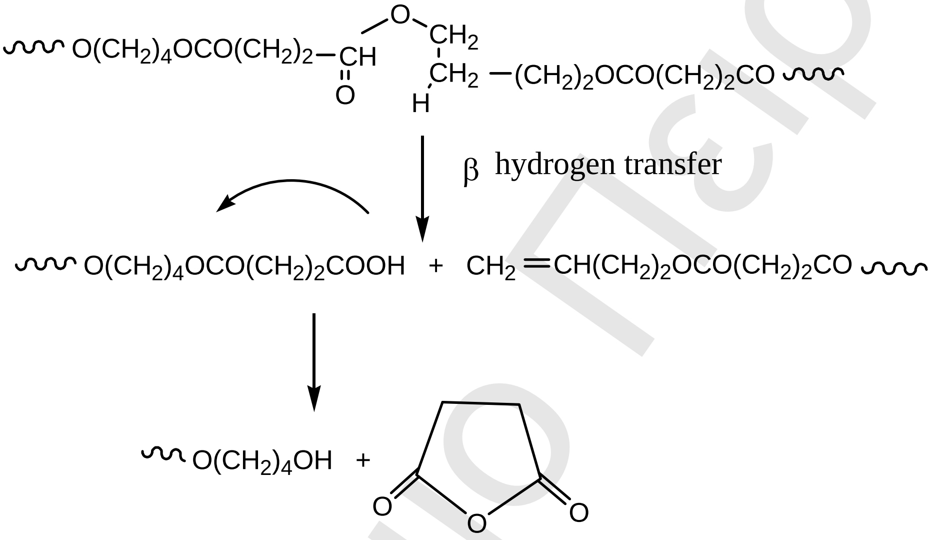
Both in nitrogen and in air, the temperatures of the beginning of degradation of the copolyesters PBSF are lower than the corresponding temperature for PBS. Moreover, their stability increases with increasing fumarate content. Also, the copolyesters are more stable in air than in nitrogen and this can lead to the conclusion that oxygen inhibits the thermal degradation reactions and that these inhibitory reactions take place at the double bonds. The thermogravimetric analysis curve of PBS reveals that this polyester shows weight loss of 5, 50, and 90% at 325, 400, and 424°C, respectively, in air. It should be noted that this does not indicate that PBS polymer chains are thermally stable up to 325°C [74].

5.1.4. Thermal degradation of PBS and Its Copolymers

Rizzarelli et al [161] examined the thermo-oxidation mechanisms of commercial PBS polyesters. Thermal oxidation was performed for 0.5, 1, 2, 2.5, 3,3.5, 5 and 6 h at 170 ^{o}C, in atmospheric air and thermal degradation procedure took place under nitrogen flow at 240 ^{o}C for 60, 75, 90,105,120 and 135 min, at 250 and 260 ^{o}C for 1 h. The results obtained showed that thermal oxidation produces a significant reduction of the molar mass of the polyesters, promoting the formation of PBS oligomers with different end groups. The identification of the structures and end groups attached to the oligomers produced is really important, since the end groups reveal the particular mechanism that has been active in the thermal degradation.

The initial step in this process consists of a hydrogen abstraction from the methylene group adjacent to the ester linkage, leading to the formation of a hydroperoxide intermediate. Remarkably, the hydroperoxide intermediate (I) decomposes by radical rearrangement reactions via the hydroxyl ester (III) or from the radical (II) which may follow two different pathways. These three degradation pathways have been revealed to be time-resolved, showing a different induction period.

Thermal degradation experiments were also performed showing a decomposition pathway through a b-hydrogen-transfer bond scission, followed by the production of succinic anhydride from succinic acid end molecules via a cyclisation decomposition mechanism.



Scheme 5.1. Thermal degradation mechanism of PBS [161]

PBS presents a good thermostability since no significant weight loss, 0.8% for PBS, occurred until 300 ^{0}C. From preliminary studies of the monomers, it was found that succinic acid degrades at temperatures close to 200 ◦C while butylene glycol evaporates at slightly higher temperatures, nevertheless lower than 300 ^{0}C. Consequently, it can be concluded that the number of methylene groups of used diol for polyester preparation has a crucial effect on its thermal stability. As the number of methylene groups increases, thermal stability decreases [54]. The thermal degradation temperatures of PBS are almost the same in nitrogen and air [74]. The mechanism of thermal degradation however should be examined not only as a degradation route but as a way to synthesize new compounds, including polymers, oligomers, and monomers.

5.2. PBS recycling techniques

Majority of plastic processing companies recycle in-house thermoplastic scrap, which is produced as sprues, offcuts or trimmings. Most of this material is re-worked as addition to virgin feedstock, while a number of reactions take place, which are detrimental to the properties of a polymer.

These may be oxidation, cross-linking, decomposition and molecular mass reduction. To reduce degradation, anti-oxidant and stabilizers are used, either identical to those used in the original material, or if new applications are envisaged, those appropriate to the new use. Lower grade scrap, which is dirty, contaminated and consists of mixed colors but is single polymer type, may be converted to low grade colored or filled compounds, suitable for use in many standard fabrication processes. Similarly, thermoset waste can be used but only as ground or shredded fillers. The recycling of polymer materials is of increasing importance nowadays. The main polymers recycling techniques are mechanical recycling, chemical recycling and incineration.

Generally, for any viable and sustainable recycling processthe following criteria must be satisfied:

- consistent and abundant supply of feedstock
- materials must not be necessarily monopolymeric or uncontaminated
- existence of a significant economic advantage in using recycled materials
- reprocessing technology must be developed and available
- there must be market for the new products

5.2.1. Mechanical recycling

Among the methods referred above, there have been several reports that suggested material recycling as one of the most efficient and reliable methods to deal with polymers recycling, since direct reprocessing can be efficiently carried out [162, 163].

The mechanical recycling process involves several steps: separation of plastics by resin type, washing to remove dirt and contaminants, grinding and crushing to reduce the particle size, extrusion by heat and reprocessing into new plastic goods. Mechanical recycling of plastics is limited by the compatibility between the different types of polymers because this can cause dramatically changes in new polymer properties and therefore applications. Another problem with mechanical recycling is the presence in plastic addition, most polymers suffer certain degradation during their use due to effects of temperature, ultraviolet radiation oxygen and ozone. That is the reason for lower properties and performance of recycled polymers comparing with the virgin onew.

Kanemura et al. [126] examined PBS as a promising biodegradable and reprocessable material used for material recycling in water. It turned out that using the biodegradable PBS could induce the total reduction of the environmental burdens in the material recycling, where uncollected waste, discarded materials and material losses can eventually biodegrade to reduce the overall environmental load. Moreover, it was found that the mechanical properties of PBS were enhanced after reprocessing, which could not be observed in other types of biodegradable materials such as PLA.

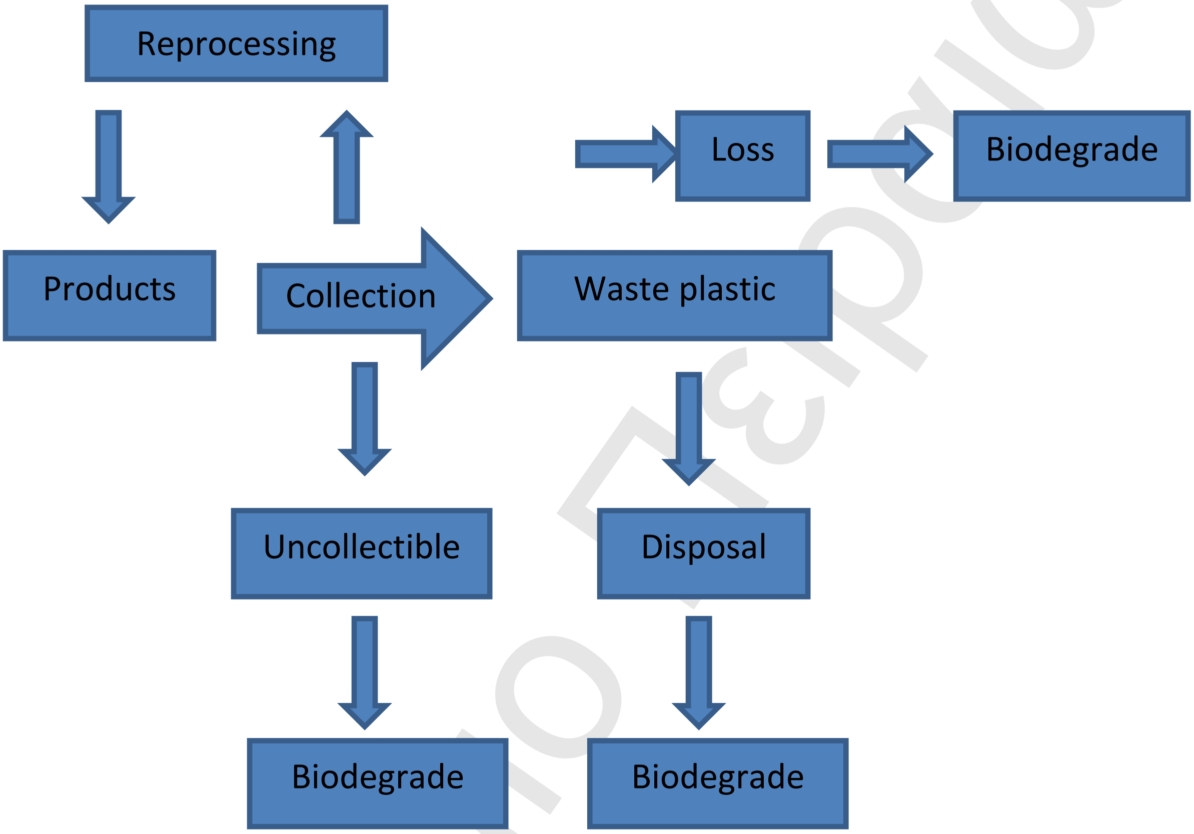


Figure 5.1. Biodegradable material recycling [126]

More specifically, the effects of the reprocessing properties of PBS in water are affected as preseted below:

- According to the results of the three-point-bending test, there was hardly any degradation observed PBS up to the third reprocessing cycle at 140^{o}C. When immersed to water, on the contrary, the molecular weight of PBS was reduced due to the chemical degradation. However, the molecular weight of the immersed PBS became higher after reprocessing, indicating the cure of the chemical degradation owing to the re-synthesis of the PBS during the reprocessing.

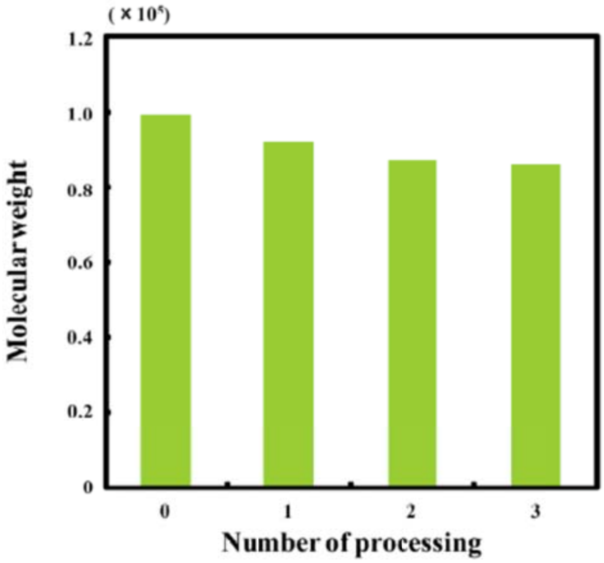


Figure 5.2. PBS homopolymer Mw against the number of reprocessing without water [126]

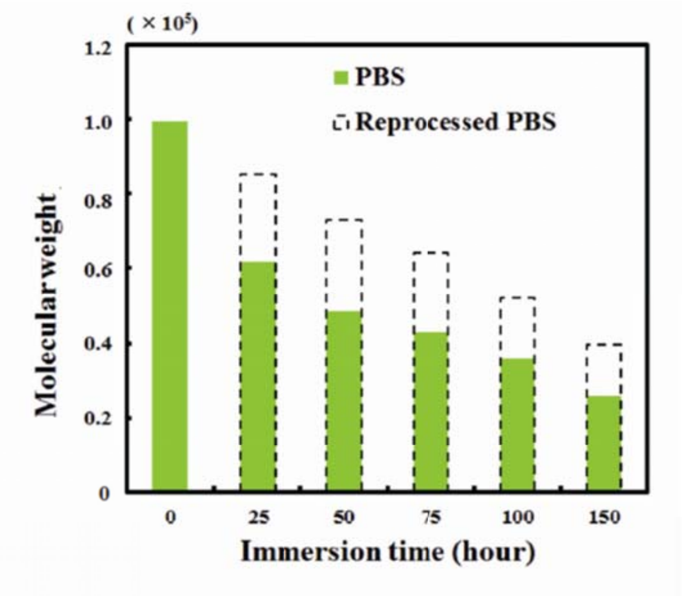


Figure 5.3. PBS Mw against immersion and reprocessing [126]

- The bending strength of PBS materials immersed in water at high temperature decreased as the immersion time increased. Degradation was caused by hydrolysis due to the immersion which eventually affected the bending strength. Concerning the reprocessed material after immersion its bending strength was higher than that of the immersed one. This improvement is possibly due to the removal of the cracks and voids that have been created on the surface of the degraded PBS.

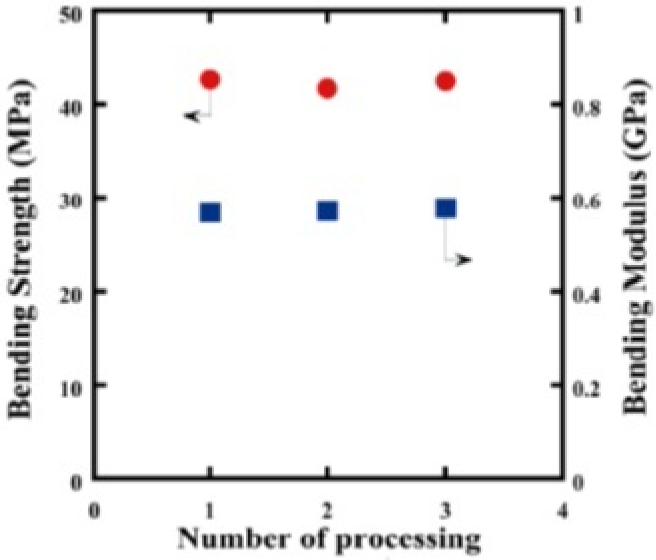


Figure 5.4. The bending properties of PBS against the number of reprocessing [126]

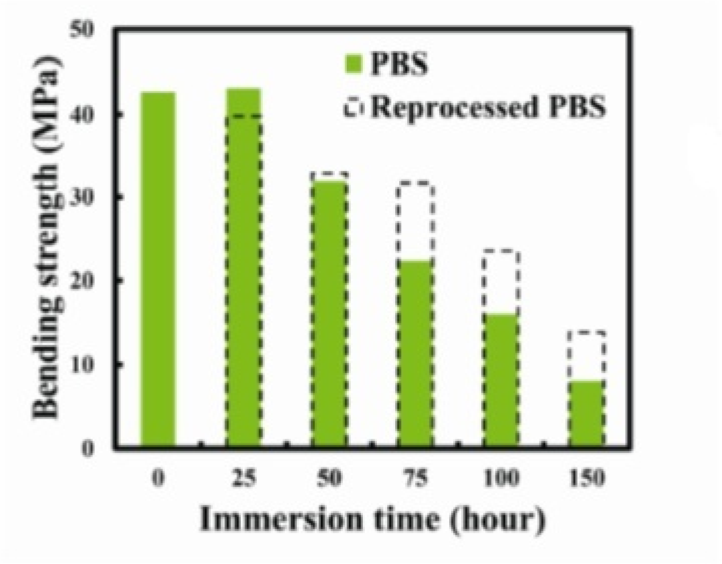


Figure 5.5. The bending properties of PBS against the number of reprocessing [126]

5.2.2. Chemical recycling

Chemical recycling also know as feedstock or tertiary recycling is a method based on the decomposition of polymers by means of heat, chemical, or catalytic agent in order to yield a variety of products ranging from the chemical monomers to a mixtures of compounds. Nevertheless, feedstock recycling is more limited by process economy than by technical reasons. The profitability of the technique is mostly determined by the degree of separation required in raw wastes, the value of the products obtained, and the capital investments in the processing facilities. Chemical (monomer) recovery is totally effective for the recycling of biodegradable plastics and specially polyesters like PBS, which easily undergo hydrolysis and decompose into monomers such as organic acids and polyols.

During the chemical depolymerization process, the polymer is cracked to the original monomer in the presence of different reagents. Recycled monomers are identical to those used in the preparation of virgin polymers. Chemical depolymerization is the most established method of plastic feedstock recycling, even though it is restricted to the recycling of condensation polymers and there are no applications of decomposition of other polymers. Depending on the chemical agent used to break down the polymer, different depolymerization routes are envisaged: for instance glycolysis, methanolysis, hydrolysis and ammonolysis.

Thermal treatment is a collective term to describe different methods and processes developed for breaking down polymeric materials simply by treatment at high temperature in an inert atmosphere. They are mainly used for the feedstock recycling of addition polymers, whereas condensation polymers are preferably depolymerised by reaction with certain agents. Thermal degradation of plastics and rubber proceeds through a radical mechanism, which may involve three different pathways:

- Random scission leading to the formation of smaller polymeric fragments as primary products
- End-chain scission, where a small molecule and a long-chain polymeric fragment are formed.
- Abstraction of functional substituents to form small molecules

In many cases, several of these pathways occur simultaneously. During the thermal degradation of many polymers, other reactions may also occur at the same time.

PBS being a biodegradable polyer and due to its high hydrolyzability in the presence of water has a high potential for monomer recovery by hydrolytic degradation after its use. However, monomer recovery through hydrolytic degradation in the solid state should be avoided because the highly hydrolysis resistant crystalline residues (or extended chain crystallites) are formed and their very slow degradation will cause low monomer yield in a limited short period or will take a long time to give a high yield. Fir this reason hydrolytic degradation of biodegradable polyesters in the melt das been developed.

Tsuji et al. [149] have examined hydrolytic degradation of PBS and PBSA as a recycle/recovery method. At degradation temperatures of 250–300 °C, the yields of succinic acid and of butanediol reached about 65–80 % and 30 %, respectively, although the total organic carbon (TOC) values reached about 90 % of the theoretical values. Low monomer yields or differences between TOC and monomer yields are probably a result of the decomposition of the formed monomers. However, it is believed that a further optimization of hydrolytic degradation conditions will result in higher monomer yields.

Enzymes are also used for chemical recycling of plastics. The substrate specificity of enzymes may be the most excellent feature although it is also important in that reactions can be carried out at normal temperature and under normal pressure, thereby saving energy costs and requiring no organic solvent responsible for environmental pollution. In general, bioprocesses require high costs and hence are disadvantageous in this point without any doubt, but it is a great merit to achieve extraction of high purity monomers without separation. To establish enzymatic recycling, the premise is the presence of a strong plastic degrading enzyme.

Nakajima et al. [155] have made several experiments on findind the appropriate enzyme for polymer decomposition and monomer recovery for PBSA. Biodegradable plastics are most suitable for biochemical monomer recycling because they must be degraded by specific enzyme containing environmental microorganisms as it is already presented in paragraph 5.1.2. Indeed, there have been many reports regarding the isolation of bacteria and fungi that can degrade these plastics from various environmental sources. Most reported PBSA-degrading microorganisms, however, can only degrade emulsions or films (with thickness b50 ìm) but not solid plastics. Nakajima screened and identified a novel bacterium that has high PBSA monomerization activity. Strain TB-71 could completely monomerize the solid PBSA. The amounts of succinic acid and adipic acid, however, were much lower than that of butanediol.

In recent years another method receiving much attention for recycling polymers is degradation performed under sub- and supercritical water conditions. In experiments held by the Kasetsart University within a thesis, [164] succinic acid and butanediol were extracted using different adsorbents for polar extraction, namely silica gel, florisil and polystyrenedivinyl benzene (PSDVB) as solid phase to extract the degraded components. It was found that the PSDVB solid phase was chosen for extraction of succinic acid and butanediol degraded products because of thier higher extracted yield from aqueous matrixes than those obtained from silica gel and florisil. The advantages of the method are usage of environmental friendly solvent, low organic solvent consumption, cheap and non-toxic reagent, relatively simple equipment, and an ease in further product recycling.

At last, great attention should be paid concerning PBS recycling in order to be used for packaging. Any polymer whether virgin or recycled must meet the appropriate standards for food contact. Thus, the recycling process must not only produce reconstituted polyester with appropriate physical and chemical characteristics, but moreover be sufficiently pure to meet food quality standards. According to patent EP 1084171B1 [165], a method of recycling PBS and other polyesters of sufficient high purity to meet food packaging requirements is consisting from the follow steps:

- Extruding a melt of cleaned post consumer polyester
- Solidifying and pelletizing the post consumer melt
- Blending the post consumer polyester with virgin polyester prepolymer resin
- Polymerizing the blend in solid state

5.2.3. Incineration

Incineration of polymers can also be seen as a recovery method since plastics could replace the application of other oil based fuels. It can be viewed that the plastic application is the first purpose of oil, and energy production is the secondary task. Indeed incineration with energy reclamation is considered as a recovery method and, due to their high energy content, polymers are valuable fuels.

As a result of the combustion, several non combustible gases and vapors can evolve, such as volatile low-melting heavy metals and a wide variety of acid gases.If these gases are discharged uncontrolled into the atmosphere along with the fly ash they can constitute a high level of emission leadin to global warming and pollution. A well-operated incinerator can virtually eliminate most of the fly ash and whatever hazardous chemicals adhere to the ash.

Incineration process however has the advantage that the plastics have high calorific value. For this reason incineration plants have to be modified for efficient combustion of the polymers and regulation of the gas emissions to ensure that no toxic gases are released. Energy recovery through incineration is an essential part of an overall waste management scheme [166].

Concerning PBS, it can be incinerated with less problems to the furnace as its combustion heat is relatively low and does not generate toxic or acid gases. Specifically, when incinerated, the heat of combustion and the generation of carbon dioxide are about one half and two thirds of conventional polyolefin respectively. Scientists having studied PBS behavior think that this polymer is better than PE for incineration since it has lower BTUs.

CONCLUSIONS

Poly(butylene succinate) (PBS) and its copolymers are a family of biodegradable polymers with excellent biodegradability, thermoplastic processability and balanced mechanical properties. In this paper, production of the monomers succinic acid and butanediol, synthesis, processing, properties and recycling of PBS and its copolymers were reviewed. The main coclusions after studying and reviewing the bibliography are the following:

- Physical properties and biodegradation rate of PBS materials can be varied in a wide range through copolymerization with different types and various contents of monomers

- PBS has the best processability among the general degradable polymers. Due to its wide temperature window for thermoplastic processing, the resin is suitable injection molding, extrusion molding or blow molding using conventional polyolefin processing equipment, lowering barrier to switch to PBS from other polymer

- Mechanical properties of PBS are almost the same with polyethylene and polypropylene so it can satisfy the general requirements for use in plastics

- PBS's thermal deformation temperature is approximately 100°C which can be increased after property alteration. PBS has a good heat resistance performance compared to other fully biodegradable polymers and is able to meet the heat resistance requirement of daily articles, such as cold/hot drink packaging and food containers

- PBS is basically stable in the atmosphere but biodegradable in soil, seawater and compost. It can maintain a stable performance in a relatively long storage and usage period while being degraded quickly after use

- PBS has great flexibility and it has emerged as a biodegradable material potentially for a wide range of applications, such as packaging materials, food containers, packaging films, garbage bags, disposable medical devices, hygiene products, textiles and covering materials for landscaping purposes. It can also be blended with other compounds, such as starch and adipate copolymers, enabling a more economical use

PBS copolymers are fully biodegradable synthetic aliphatic/aromatic copolyesters having a melting point between 100°C and 120°C and are in solid form under room temperature. Comparing to to PBS homopolymer, PBS copolymers have the following characteristics:

- Enhanced tensile strength and tear strength so that the packaging bag made by PBS copolymer can carry heavier weight and be re-used
- Higher transparency and suitable for use in the packaging of food and cigarette and as advertising materials
- Improving the compatibility of degradable polymers with other materials, such as starch, PLA and PHB so that the toughness and processability of the mixed degradable materials will be enhanced.

Therefore, PBS copolymers are believed to be the most suitable degradable material to be used in packaging, films and fibre materials in terms of its mechanical properties and processability.

At the present stage, petroleum or coal based succinic acid is still cheaper than bio-based feedstock. With future development of fermentation technology and the finding of new microbial strains, bio-based succinic acid will become competitive and so PBS will be one of the most preferable biodegradable polymers especially for packaging applications.

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