

# Biodegradable Polymers Available On The Market

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## Abstract

The growing attention from the public opinion towards protecting the environment has enormously increased interest in biodegradable polymers, increasingly used in packaging, agriculture, medicine and many other sectors.

Two classes of biodegradable polymers can be distinguished: synthetic polymers and natural polymers.

Biodegradable synthetic polymers can be produced from either raw materials derived from petroleum resources (non-renewable resources) or biological resources (renewable resources), or a combination of both.

Natural polymers as such or partially modified, are extracted from materials found in nature. In general, natural polymers offer lower performance than synthetic polymers.

Below is an overview of the different biodegradable polymers on the market and their properties, as well as information on their synthesis and properties.

**Keywords:** biodegradable polymers, polyesters, polyhydroxyalkanoates, biopolymers.

## Introduction

The main property of plastics (synthetic polymers) is their durability which makes them ideal for multiple applications such as packaging, building materials, commodities, hygiene products, etc. but that brings with it, at the end of the life of the product, problems of waste disposal. In fact, traditional plastics derived from petroleum are not easily biodegradable, due to their resistance to microbial biodegradation, and therefore accumulate in the environment.

This problem, combined with greater attention to the environment in which we live, have helped to stimulate interest in biodegradable polymers, both synthetic and natural.

Biodegradation occurs through the action of enzymes and / or physical and chemical deterioration associated with the action of living organisms. Action thanks to which the constituent elements, the molecules or the same atoms, become available for new natural processes. This event occurs in two phases. The first is the fragmentation of polymers into lower molecular mass species by abiotic reactions, i.e. oxidation, photodegradation or hydrolysis, or biotic reactions, i.e. degradations by microorganisms. The second is the bioassimilation of the polymer fragments by microorganisms and their mineralization.

The biodegradability of a polymer does not depend on the origin of its constituents but on its chemical structure and environmental conditions. The mechanical behavior of biodegradable materials also depends on their chemical composition, production, storage and processing characteristics, aging and conditions of use.

## Biodegradable Polymers

To be biodegradable, polymers must contain on their main chain one or more hydrolyzable functions, such as eg. an ester group, amide, urethane, ...

Below we will focus our interest on industrially available biodegradable polymers that are readily commercially available in large quantities. Only in some cases, for completeness of information, we will mention some products whose commercial availability is minimal or non-existent.

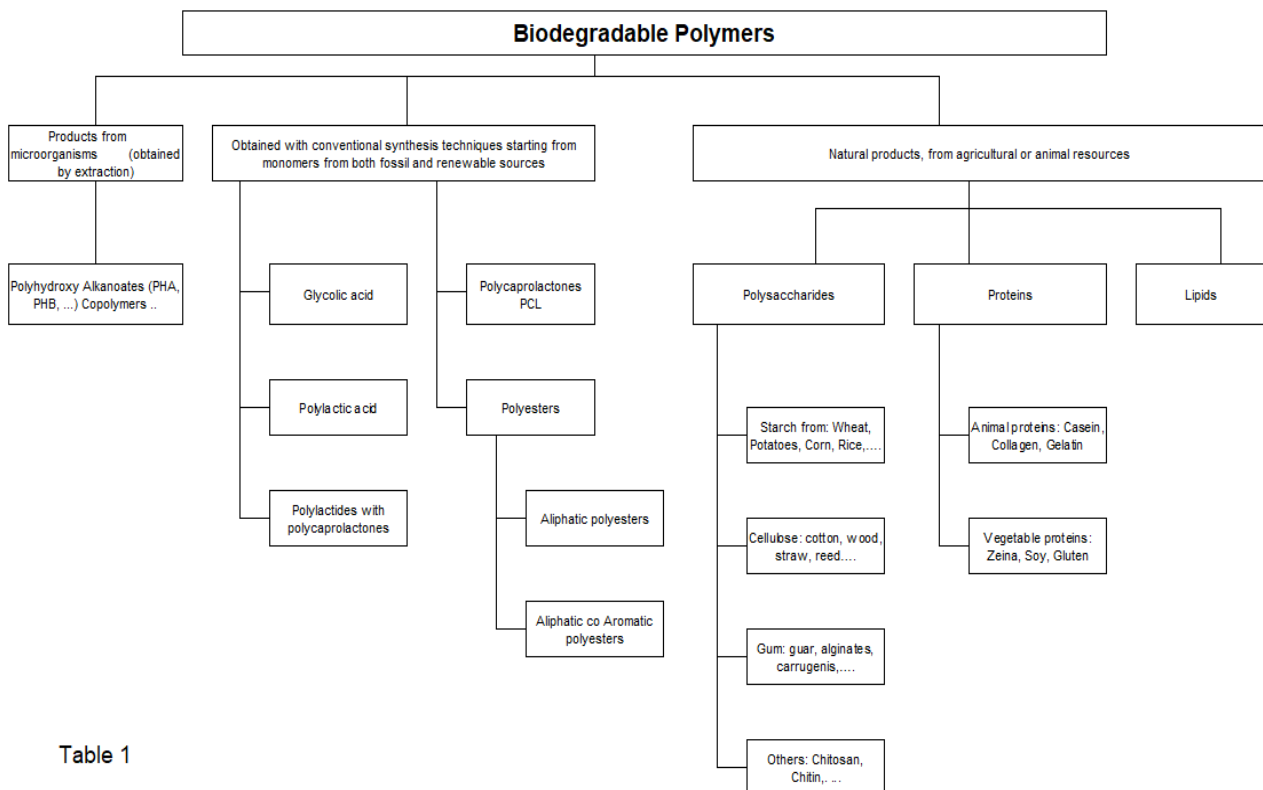


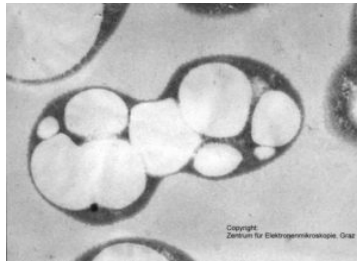
Table 1

Table 1 gives an overview of biodegradable polymers available on the market are only a small part of this table and almost entirely refer to products that have an ester group on the main chain.

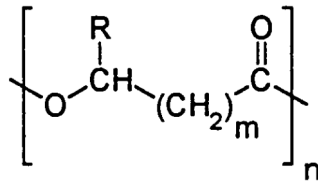
Let's start with polyhydroxyalkanoate.....

## Polyhydroxyalkanoates

Polyhydroxyalkanoates are thermoplastic polymers synthesized by various types of bacteria (Bacillus, Rhodococcus, Pseudomonas, etc.) by fermentation of sugars or lipids. These polymers represent a carbonaceous reserve for bacteria which, especially in particular cultivation conditions, such as the absence of certain nutrients (nitrogen, phosphorus, sulfur, ..) or at high concentrations. They accumulate in the form of granules inside the bacterium itself, up to 90% of the dry weight of the bacterial mass.



These products are by their nature 100% biodegradable and obviously obtained from 100% renewable sources. The general structural formula of these materials is:



Given the great variability of the side chains (-R) and the length of the main chain (m), polyhydroxyalkanoates have very variable physical and chemical properties. Melting points between 40 and 180 ° C and physical-chemical properties ranging from those typical of thermoplastic polymers to those typical of rubbers (elastomers).

Let's see some of the polyhydroxyalkanoates obtained both by bacterial and chemical synthesis

If R=H and m=0		Poly (glycolic acid) <b>PGA</b> Dexon (1962)
If R=H and m=1		Polyhydroxypropionate
If R=H and m=2		Poly 4 hydroxybutyrate
If R=H and m=4		Polycaprolactone <b>PCL</b>
If R=CH <sub>3</sub> and m=0		Polylactic acid <b>PLA</b>
If R=CH <sub>3</sub> and m=1		Poly 3 hydroxybutyrate
If R=CH <sub>2</sub> -CH <sub>3</sub> and m=1		Polyhydroxyvalerate <b>PHV</b>
If R=CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> and m=1		Polyhydroxyhexanoate <b>PHH</b>
<b>Copolymers available industrially</b>		
		Enumat Y100P TianAm Biopolimer <b>PHBV</b>
		Aonilex Kaneka <b>PHBH</b>

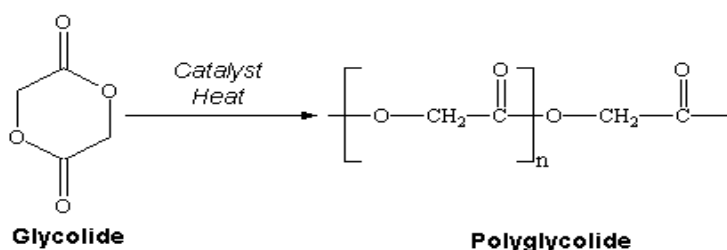
Below are some data relating to the properties of the two copolymers (PHBV and PHBH) available industrially, as reported in the technical data sheets of the manufacturers.

Properties	Analytical method	Unit of measure	PHBH			PHBV
			X151A	X131A	X331N	Y100P
Density	ISO 1183	g/cm <sup>3</sup>	1,19	1,20	1,20	1,25
Thermal properties						
Melting Point	DSC	°C	126	145	145	175-180
Melt flow index (165°C - 2,16 Kg)	ISO 1133	g/10 min	3	3	12	8-15
Glass Transition Temperature	DSC 20°C/min	°C	0	2	2	--
HDT (heat deflection temperature)	ISO 75,	°C	86	107	107	157-165
VICAT (softening temperature)	ISO 306, A120	°C	--	--	--	166
Mechanical properties						
Tensile yield strength	ISO 527	MPa	26	36	--	31 -36
Tensile modulus	ISO 527	MPa	950	1820	--	--
Tensile elongation at break	ISO 527	%	320	4	--	3,8
Flexural modulus	ISO 178	MPa	850	1650	1680	2200-2900
Impact resistance						
Charpy (notched)	ISO 179	KJ/m <sup>2</sup>	3	2	2	--
Izod (notched)		J/m	--	--	--	55-70
Moisture permeability	JIS Z0208	g*mm / m <sup>2</sup> *day*atm	8	5	--	--
Oxygen permeability	JIS K7126	cm <sup>3</sup> *mm / m <sup>2</sup> *day*atm	9	5	--	--
CO <sub>2</sub> Permeability	JIS K7126	cm <sup>3</sup> *mm / m <sup>2</sup> *day*atm	36	19	--	--

Sources: <http://www.kaneka.be/documents/Aonilex-Brochure-2017.pdf> ; Enmat Y1000P TDS

## PGA (polyglycolic acid)

PGA is the simplest linear aliphatic polyester. It is prepared by polymerization with the opening of the ring of a cyclic lactone, the glycolide.



The molecular weight of the repeating unit is 116, the percentage of carbon contained \* is about 41.4%. [\* For all the molecules that we will mention we will always try to indicate the percentage of carbon contained. This value is particularly important when calculating the "carbon biobased content" of carbon from renewable sources. ]

PGA has been known since 1954 [1] as a polymer capable of forming very resistant fibers, however due to its hydrolytic instability compared to other polyesters its initial use was very limited.

PGA has a glass transition temperature between 35-40 ° C and a melting temperature that can be identified between 225-230 ° C. This polymer is also characterized by a high degree of crystallinity (around 45-55%), which gives it a certain resistance to hydrolysis.

The degradation process is erosive and appears to follow two steps, during which the polymer is converted back to glycolic acid. In the first phase, the water infiltrates the amorphous non-crystalline regions of the material, splitting the ester bonds present; the second phase begins when the amorphous region has been eroded and the crystalline portion of the polymer is exposed to the action of water. When the crystal structure collapses, the polymer chain dissolves.

When exposed to physiological conditions, PGA degrades not only by hydrolysis processes, but also by some classes of enzymes, in particular those belonging to the esterase family. The degradation product, glycolic acid, is non-toxic and can enter the Krebs cycle, at the end of which it is secreted in the form of water and carbon dioxide. Some of the glycolic acid is also excreted in the form of urine. [2]

Studies conducted on sutures made of PGA have shown that the material loses half its strength in about two weeks and 100% in a month. The polymer is then completely reabsorbed by the body in a time window of 4-6 months.

This last property is the basis of its industrial development, in fact in 1962 the PGA was used to develop the first synthetic absorbable suture, patented by Davis & Geck (subsidiary of American Cyanamid co) 1963 (US 3297033) and market under trade name "Dexon". These sutures are resistant and able to degrade up to water-soluble monomers, they have had considerable success in the field of surgery, in particular for the advantage of not having to perform subsequent operations to remove the stitches. In addition to the use of PGA alone, with the aim of obtaining a material with specific characteristics,

various copolymers of polyglycolic acid have been prepared using other monomers such as for example the polyglycolic acid / dodecanol alcohol copolymer known commercially as Vicril [3]. The same PGA coated with polycaprolactone co-glycolide takes the trade name of Dexon II [4].

The copolymers have intermediate characteristics in terms of degradation rate and solubility, depending on the ratio between the various monomers used in the synthesis and on the nature of monomers itself.

Recently Pujing Chemical Industry CO., LTD presented Vytal-J226 a grade to be used for injection molding with the following properties, reported in their data sheet.

Properties of the Vytal-J226 are reported in their data sheet

Properties	Analytic Method	Unit	Value
Appearance			Yellow to brown chips
moisture content	Karl-Fischer method	ppm	<400
Melt index	ISO1133-1	g/10min (230°C/2.16kg)	25
Melting Point	ISO 11357-1	°C	220 °C
Glass transition	ISO 11357-3	°C	38 °C
Flexural strength	ISO 178	MPa	170
Tensile strength	ISO 527	MPa	105
Tensile modulus	ISO 527	MPa	790
Impact strength	ISO180	kJ/m	2.9

[1] C. E. Lowe: "Preparation of high molecular weight polyhydroxyacetic ester", U.S. Pat 2 668 162, 1954

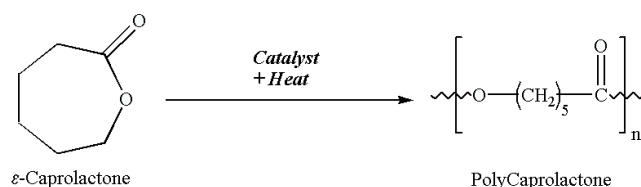
[2] Pathiraja A. Gunatillake e Raju Adhikari (2003). "Biodegradable Synthetic Polymers for tissue engineering" (PDF). European Cells and Materials 5: 1-16

[3] <http://shop.demas.it/admin/uploads/articoli/1693.pdf>

[4] <http://www.dentalcompare.com/4596-PGA-Sutures/37784-Dexon-II/>

## PCL (policaprolactone)

Polycaprolactone (PCL) is a biodegradable polyester with a low melting point, its structural formula is:



The molecular weight of the repeating unit is 114, the percentage of carbon is about 63%. The melting temperature is 57 ° C and the glass transition temperature is -60 ° C.

PCL is obtained by polymerization through the opening of the  $\epsilon$ -caprolactone ring due to heat in the presence of a catalyst, high molecular weight polymers can be obtained (eg Capa 6800 has a MW of about 7000 [5] [6] ). It is a semi-rigid material which at room temperature has a flexural modulus of about 300 MPa, low tensile strength and high elongation at break (> 800%).

Polycaprolactones have been produced for many years and have various uses, the most important of which are in the medical field, as additives for polyurethanes, as polymeric plasticizers for PVC, etc.

Since they are easily biodegradable, they were initially also used for the production of films (eg take-away bags) however this use was soon abandoned due to their low melting point. To partially solve this problem, PCL is often used in a mixture with PLA, PGA, starch, etc. since it brings high elongation at break to alloys.

PCL is commercially available under various trade names CAPA® (from Solvay, Belgium), Tone® (from Union Carbide, USA) or Celgreen® (from Daicel, Japan).

PCL degrades by hydrolysis of its ester bonds under physiological conditions (such as in the human body) and has therefore received much attention for use as an implantable biomaterial.

Its use as a biopolymer beyond medical applications is limited to blends.

[5] [https://www.tri-iso.com/documents/Ingevity\\_CAPA\\_6800\\_TDS.pdf](https://www.tri-iso.com/documents/Ingevity_CAPA_6800_TDS.pdf)

[6] [https://www.tri-iso.com/documents/Physical\\_Properties\\_o%20Capa\\_of\\_Resins.pdf](https://www.tri-iso.com/documents/Physical_Properties_o%20Capa_of_Resins.pdf)

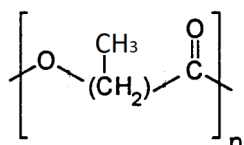


## Analytical data of Capa 6400, 6500 e 6800

Property	Analytic method	Unit	Capa 6400	Capa 6500	Capa 6800
Mean molecular weight Mn	GPC,THF, tre misura	g/mol	33000 ± 1500	49000 ± 2500	69000 ± 3500
Weighted molecular weight Mw	GPC,THF, tre misura	g/mol	45000 ± 1500	69000 ± 3500	11200 ± 5500
Polydispersity (Mw/Mn)			1,4	1,4	1,6
Specific gravity		g/cm <sup>3</sup>	1,15	1,15	1,15
Proprietà termiche					
Melting Point	DSC 5°C/min	°C	60 ± 2	60 ± 2	60 ± 2
Heat of fusion ΔH	DSC 5°C/min	J/g	80 ± 2	75 ± 2	70 ± 2
Crystallinity	DSC 5°C/min	%	52 ± 2	48 ± 2	44 ± 2
Crystallization temperature	DSC 5°C/min	°C	26 ± 1	23 ± 1	23 ± 1
Glass transition	DSC 20°C/min	°C	-60 ± 2	-60 ± 2	-60 ± 2
HDT (heat deflection temperature)	ISO 75, B120	°C	50 ± 2	51 ± 2	50 ± 2
VICAT (softening temperature)	ISO 306, A120	°C	56 ± 1	57 ± 1	57 ± 1
Tensile Properties					
Yield stress (50mm/min)	ISO 527	MPa	17 ± 1	15 ± 1	14 ± 1
Modulus (0,25 mm/min)	ISO 527	MPa	360 ± 50	300 ± 50	300 ± 50
Stress at break (50mm/min)	ISO 527	MPa	20 ± 2	55 ± 5	70 ± 5
Nominal strain at break (50mm/min)	ISO 527	%	400 ± 50	1200 ± 50	1200 ± 50
Impact toughness					
Charpy (notched)	ISO 179-1	KJ/m <sup>2</sup>	2,6 ± 0,5	11,4 ± 0,3	63,0 ± 2,3
Hardness					
Shore D	ISO 868		53 ± 1	47 ± 1	49 ± 1
Viscosity:					
70°C, 10s <sup>-1</sup>	70°C, 10s <sup>-1</sup>	Pa*s	770 ± 20	4100 ± 180	18000 ± 800
100°C, 10s <sup>-1</sup>	100°C, 10s <sup>-1</sup>	Pa*s	290 ± 10	1700 ± 50	9000 ± 400
150°C, 10s <sup>-1</sup>	150°C, 10s <sup>-1</sup>	Pa*s	95 ± 5	590 ± 15	3900 ± 130
Melt flow index					
80°C - 2,16 Kg	D 1238	g/10 min	16	2,5	0,3
160°C - 2,16 Kg	D 1238	g/10 min	> 75	18	2,4
190°C - 2,16 Kg	D 1238	g/10 min	N/A	30	4,1

## PLA (polylactic acid)

PLA is a linear aliphatic polyester, its chemical structure is:



The molecular weight of the repeating unit is 72 of which the percentage of carbon is 50% by weight. CAS number 26100-51-6

PLA was first made in 1931 by Du Pont scientist Wallace Carothers by heating lactic acid in a vacuum. However, the difficulty in obtaining high molecular weights only with vacuum heating and the subsequent tendency of the product to degrade made the product temporarily set aside.

Normally the monomer, lactic acid (2-hydroxy propionic acid), is obtained from corn starch or sugar cane by chemical synthesis or fermentation. Fermentation is carried out by defined lactic bacteria such as *Streptococcus*, *Pediococcus* and *Lactobacillus* on glucose or other fermentable sugar (molasses, beets, sugar cane ...), in the absence of oxygen. Bacteria transform sugars into pyruvic acid  $\text{CH}_3\text{COCOOH}$  ... which is subsequently reduced to lactic acid.

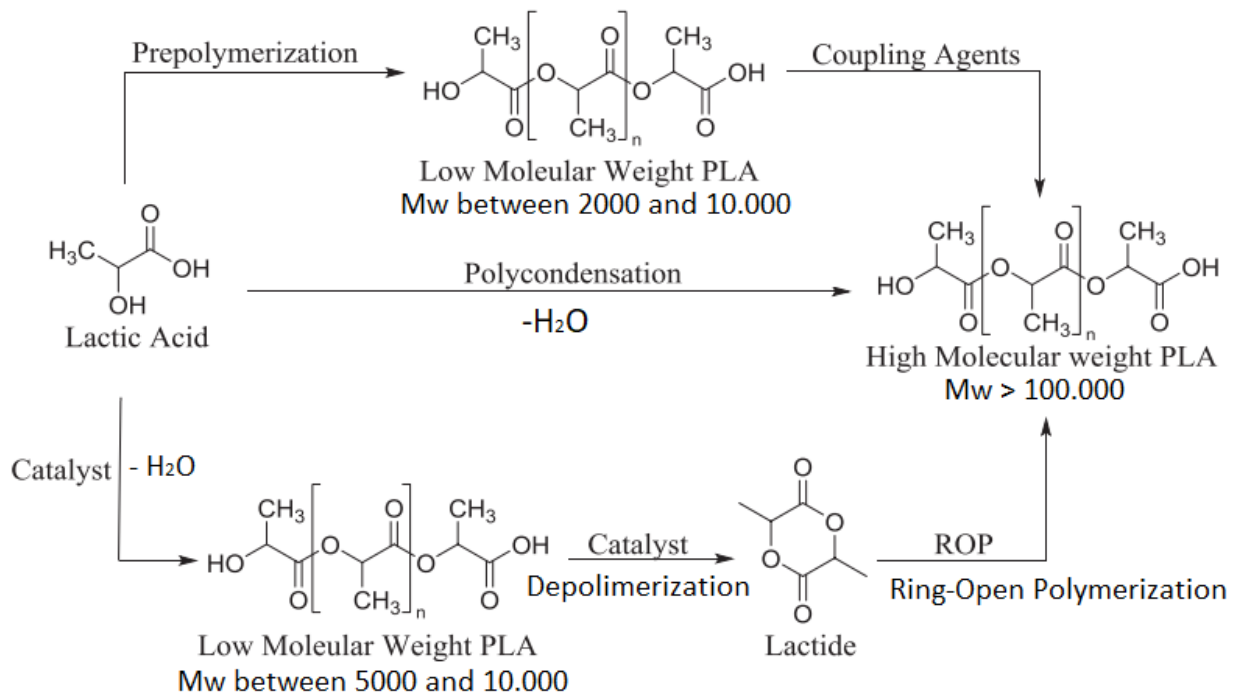
The lactic acid produced by fermentation by microorganisms is optically active, the stereoisomers L (+) and D (-) can be obtained using the appropriate lactobacillus.

High molecular weight PLA can be produced in two different ways. One method is condensation polymerization in which water is removed by vacuum solvent pushed to a certain temperature.

The other method is ring opening polymerization of 2.5 dimethyl 3.6 diox or 1.4 dioxane (Lactide).

The following diagram shows the synthesis methods for obtaining PLA with a high molecular weight. At an industrial level, only ring-opening polymerization of lactide is used.

There are four forms of PLA that can be obtained from the different types of lactide. L-PLA and D-PLA are the two optically active regular forms, prepared starting from L-lactide and D-lactide, the other two optically inactive forms are: L, D-PLA obtained from the mixture of L-lactide and D-lactide, and the meso-PLA form. Depending on the ratio of monomers D (-) and L (+), PLA can be modified from totally amorphous up to a crystallinity of about 80%. It has been found that PLA with a percentage greater than 93% of isomer L or conversely of isomer D has a semi-crystalline behavior while PLA contains mixtures of D and L outside these limits is substantially amorphous.



PLA is one of the most promising biopolymers on the market and has a wide range of applications ranging from food packaging, biodegradable bags, disposable tableware, TNT (non-woven fabric), to biomedical applications. However, some properties such as low impact resistance, low elongation at rupture, poor barrier properties, low crystallization rate but above all the low deflection temperature under load, HDT, hinder its development in a number of applications. Large-scale industrialists of the PLA.

Many studies have been conducted to try to overcome the aforementioned limits of PLA, one method is to increase the percentage of crystallinity, another (perhaps the most followed) is to mix PLA with other polymers (blending) in order to obtain materials with the desired properties.

However, the low tendency of crystalline PLA to degrade hinders its diffusion as a biodegradable and compostable material.

[http://www.natureworksllc.com/~media/Files/NatureWorks/Technical-Documents/Technical-Data-Sheets/TechnicalDataSheet\\_8052D\\_foam\\_pdf.pdf](http://www.natureworksllc.com/~media/Files/NatureWorks/Technical-Documents/Technical-Data-Sheets/TechnicalDataSheet_8052D_foam_pdf.pdf)

Properties	Analytical method	Unit	INGEO PLA 2003D [1]	CORBION Luminy LX 175 [2]	CORBION Luminy D 120 [3]
Densità	ISO 1183	g/cm <sup>3</sup>	1,24	1,24	1,24
Melt Flow Index	ISO 1133 190°C 2,16Kg	g/10min	2	3	10
Melt Flow Index	ISO 1133 210°C 2,16Kg	g/10min	6	8	23
Melting point	DSC	°C	160	155	175
Yeld Stress	ISO 527-1	MPa	60		
Stress at Break	ISO 527-1	MPa	53	45	
Elongation at break	ISO 527-1	%	6	5	5
Tensile modulus	ISO 527-1	MPa	3500	3500	3500
Flexural modulus	ISO 178	MPa			
Flexural strength	ISO 178	MPa			
Izod Notched	ISO 180	J/m	16		
Charpy Notched	ISO 179-1	KJ/m <sup>2</sup>		5	5
HDT 0,45MPa 120°C/h	ISO 75-2	°C	55	55	55
Percentage of L isomer			>96%	>96%	< 0,5%
Molecular weight			101000	75000	

[1] [http://www.natureworksllc.com/~media/Files/NatureWorks/Technical-Documents/Technical-Data-Sheets/TechnicalDataSheet\\_2003D\\_FFP-FSW\\_pdf.pdf](http://www.natureworksllc.com/~media/Files/NatureWorks/Technical-Documents/Technical-Data-Sheets/TechnicalDataSheet_2003D_FFP-FSW_pdf.pdf)

[2] <http://www.corbion.com/media/442336/pds-purapol-lx175.pdf>

[3] <https://www.total-corbion.com/media/0mxj0y1o/pds-luminy-d120-190507.pdf>

[4] Talita Ferreira Cipriano et al. "Thermal, Rheological and Morphological Properties of Poly (Lactic Acid) (PLA) and Talc Composites" *Polímeros*, vol. 24, n. 3, p. 276-282, 2014  
[http://www.scielo.br/pdf/po/v24n3/aop\\_polimeros1532.pdf](http://www.scielo.br/pdf/po/v24n3/aop_polimeros1532.pdf)

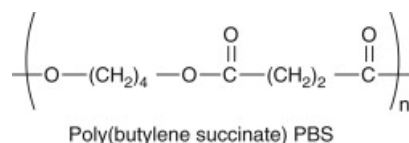
In addition to the polyesters already seen whose monomers are generally all obtained from renewable sources, there are other polyesters of industrial importance whose monomers are wholly or partly obtained from fossil sources. These are the PBS, the PBSA, the PBAT and the PBST. Among these, the polymer that is enjoying the greatest industrial interest is PBAT, whose worldwide production capacity is constantly expanding.

Chain composition	Type	Polyester	Synthesis method
Aliphatic	homopolymer	Polyglycolic acid (PGA)	Polycondensation of glycolic acid
		Poly(lactic acid (PLA)	Ring-Opening polymerization (of lactide)
		Polycaprolactone (PCL)	Ring-Opening polymerization (of caprolactone)
		Polyhydroxyalkanoate (PHA)	
		Polyhydroxybutyrate (PHB)	
	Copolymer	Polyethylene succinate(PES)	Polycondensation of succinic acid with 1,2 ethanediol
		Polybutylenesuccinate (PBS)	Polycondensation of succinic acid with 1,4 butanediol
		Polyethylene succinate-co-adipate (PBSA)	Polycondensation of succinic acid, adipic acid with 1,4 bitanediol
		Poly (3-hydroxybutyrate-co-3 hydroxyvalerate) (PHBV)	
	Poly (3-hydroxybutyrate-co-3 hydroxyhexanoate) (PHBH)		
Partially aromatic	Copolymer	Polybutylene adipate terephthalate (PBAT)	Polycondensation of terephthalic acid, adipic acid with 1,4 butanediol
		Polybutylene sebacate terephthalate (PBSeT)	Polycondensation of terephthalic acid, sebacic acid with 1,4 butanediol

Let's start with totally aliphatic products: PBS, PBSA

## PBS (polybutylene succinate)

PBS is a biodegradable linear polyester whose structural formula is:



The molecular weight of the repeating unit is 172 um and it is made up of 55.8% carbon. PBS has a crystallinity of 35-45%, its glass transition temperature Tg is -32 ° C and the melting point is 114-115 ° C.

### History

The synthesis of polyesters based on succinic acid was made for the first time in 1863. At that time the French professor Agostino Vicente Lourenço described in his "Recherche sur les composés polyatomiques" (research on polyatomic compounds), the reaction between succinic acid and ethylene glycol to form what I call "succino-ethylene acid". He noted that this acid loses water when heated to high temperatures (300 ° C) and that a crystalline mass is obtained after cooling. Unfortunately, Lourenço did not study the structure of the obtained material much.

Later Davidoff (1886), and then Voländer (1894) prepared this same material using different methods. This first work was continued in 1930 by Wallace Hume Carothers (El du Pont de Nemours and Co.), with a systematic study of succinic acid-based polyesters. At that time the aim of the researchers was to find a synthetic fiber alternative to natural silk.

Carothers, eliminating water with a continuous distillation process, obtained polymers with molecular masses higher than those previously obtained.

However, the characteristics of the final products did not give the properties then sought, and for this reason Carothers turned his attention to polyamides inventing Nylon 6,6 with his colleague Julian Hill.

Flory (1946) had instead proposed a better synthesis of aliphatic polyesters starting from diacid chlorides.

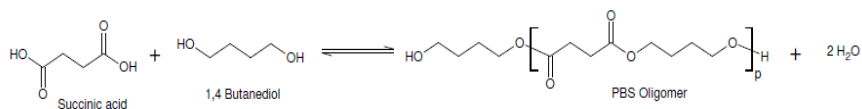
In the early 1990s, after being forgotten for more than 40 years, this polymer received renewed interest due to the growing demand for biodegradable polymers.

The Japanese company Showa Denko built in 1993 a semi-commercial plant capable of producing 3,000 tons of polymer per year. Sold under the Bionolle trade name, producing both PBS and PBSA. These polyesters were synthesized via condensed phase polymerization followed by a chain extension process with a diisocyanate.

Much later, in April 2003, Mitsubishi Chemicals built a 3,000 tons / year capacity plant and launched a PBS called GS PLA on the market. This high molecular weight polymer obtained without the use of a chain extender. Between the end of 2015 and the beginning of 2016 the MCCPTT (joint venture between the Mitsubishi Chemical Corporation (MCC) and the PTT Global Chemical Public Company Limited) in Thailand built a plant for the production of PBS starting from succinic acid from a vegetable source, thus obtaining a product with about 50% of carbon from renewable sources. This value can reach 100% with the use of 1,4 butanediol (BDO) from renewable sources.

**Production method:**

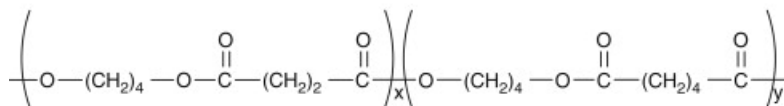
Direct esterification of succinic acid with 1,4-butanediol is the most common way of producing PBS. The synthesis consists of a two-step process. First, an excess of the diol is esterified with diacid to form PBS oligomers with the elimination of water.



Then, these oligomers are polymerized under vacuum to obtain a high molar weight polymer.

## PBSA (polybutylene succinate adipate)

However, since PBS has a lower break elongation compared to film products, PBSA was also developed by adding adipic acid in addition to succinic acid in the polymerization phase. A copolymer formed by the two acids and by 1.4 butanediol is thus obtained. This product shows various advantages in film production even though it has a melting point of only 84 degrees centigrade. PBSA has very similar properties to linear low-density polyethylene (LLDPE) and biodegrades faster than PBS, making it suitable for composting lots of kitchen waste. Its structural formula is:

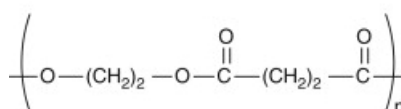


Poly(butylene succinate adipate) PBSA

### Proprietà tipiche del PBS/PBSA

Proprietà	Metodo analitico	Unità di misura	PBS grado estrusione	PBS grado stampaggio	PBSA grado estrusione
Density	ISO 1183	g/cm <sup>3</sup>	1,26	1,26	1,24
Melting Point	DSC	°C	115	115	84
Melt Flow Index	ISO 1133 -190°C 2,16Kg	g/10min	4- 6	20 - 25	3 - 5
Flexural modulus	ISO 178	Mpa	6 50	630	250
Flexural strength	ISO 178	MPa	40	40	18
Yield stress	ISO 527	MPa	39	40	27
Stress at break	ISO 527	MPa	36	30	24
Elongation at Break	ISO 527	%	210	170	380
Notched Impact Strength	ISO 179	KJ/m <sup>2</sup>	10	7	47
Vicat A/50	ISO 306	°C	≥ 80	≥ 80	
HDT B/ 0,45	ISO 75-2	°C	95	93	63
Rockwell hardness (R scale)	ISO 2039-2	-	105	105	56

There is also another polymer (PES) obtained from succinic acid and ethylene glycol which is widely discussed in the literature, whose structural formula is:



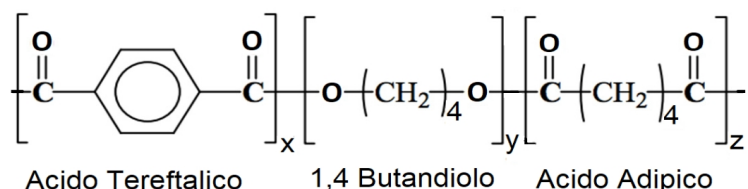
Poly(ethylene succinate) PES

The latter, however, is currently not available on the market.



## PBAT Poly (butylene adipate-co-terephthalate)

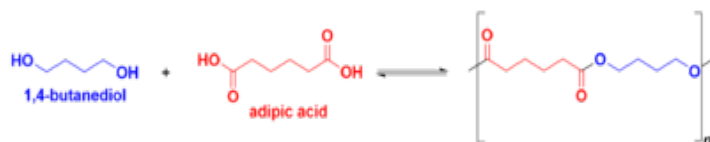
To improve the physical / chemical characteristics and reduce the production costs of aliphatic polyesters and to obtain polymers with high molecular weights, various aliphatic / aromatic co / polyesters have been studied. Among these, the most commercially successful was the PBAT. It was introduced by BASF under the trade name of Ecoflex® in 1998. The chemical structure of the PBAT is as follows:



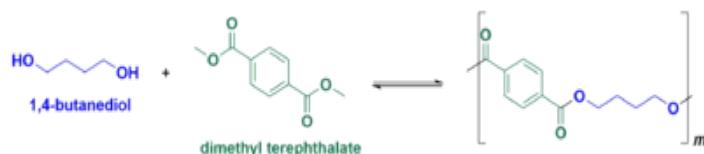
It is a random copolymer, synthesized starting from terephthalic acid, 1,4-butanediol and adipic acid. In commercial products the percentage of carbon is about 64%.

On an industrial level it is summarized in a single step. At the end of the polymerization process, a bifunctional chain extender can be added to increase the molecular weight. Or a chain extender with more than two reactive functions (3, 4, ..) to obtain a product with a higher molecular weight and with side chains along the main chain (such as low density polyethylene).

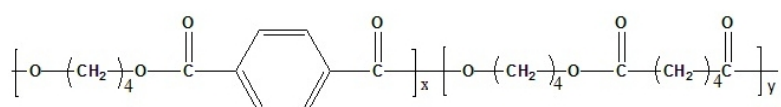
In the laboratory for simplicity it is also possible to do three steps. In the first step, 1,4 butanediol is reacted with adipic acid to obtain a linear oligomer (PBA)



In the second step 1,4 butanediol is reacted with terephthalic acid to obtain the second oligomer (PBT).



The two oligomers are then made to react with each other and a block copolymer is thus obtained.



The main role of terephthalic acid in the polymer is to strengthen the copolyester structure and facilitate the obtainment of high molecular weights. In the literature it is reported that the presence of terephthalic acid in the chain up to a maximum of 40% does not significantly alter biodegradability. In 1998, BASF presented the results on the biodegradability of Ecoflex® and stated that over 90% of this material can be metabolized within three months under composting conditions.

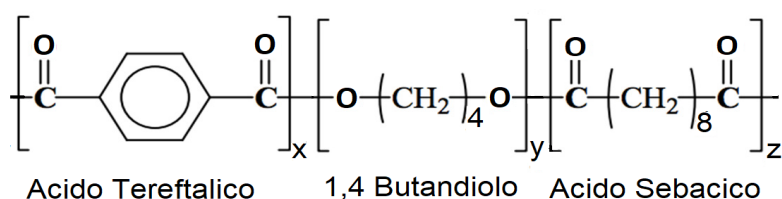
The biodegradability of PBATs was subsequently confirmed by many researchers. The glass transition temperature of PBAT is about  $-30^{\circ}\text{C}$  and the melting temperature is  $110\text{--}125^{\circ}\text{C}$ . These values offer an excellent compromise between operating temperatures and processing temperatures, the product also has excellent softness and ductility properties.

PBAT is a flexible biodegradable plastic, with mechanical properties similar to those of low density polyethylene (LDPE). This makes PBAT suitable for food packaging and agricultural film applications. However, the relatively low tensile modulus partially limits its commercial applications as is. In fact, it is generally used in blends with other biodegradable polymers (PLA, PHA, PHB, PCL, TPS, ...) and mineral fillers to obtain products that are easy to work with, with excellent physical-chemical properties and acceptable costs.

## PBST (Polibutilensebacatotereftalato)

Another polymer commercially available is PBST, although it would be better to refer to it as PBSeT. It is a modification of the PBAT in which adipic acid is replaced with sebacic acid from a vegetable source, to obtain a product partially from a renewable source.

The structural formula is:



The products available commercially are composed of a percentage of carbon from renewable sources of about 40% of the total carbon content. Novamont in various publications claims to use azelaic acid extracted from thistle, instead of sebacic acid. However, since Novamont does not sell the pure polymer, physical and chemical data of the latter product are not readily available.

### Comparison between PBAT and PBST:

Proprietà	Metodo analitico	Unità di misura	PBAT	PBST
Density	ISO 1183	g/cm <sup>3</sup>	1,24	1,24
Melting Point	DSC	°C	115 - 125	110 - 135
Melt Flow Index	ISO 1133 -190°C 2,16Kg	g/10min	2- 5	3 - 6
Flexural modulus	ISO 178	Mpa	125	80
Flexural strength	ISO 178	MPa	7 - 8	5 - 6
Notched Impact Strength	ISO 179	KJ/m <sup>2</sup>	N. B.	N. B.
Vicat A/50	ISO 306	°C	≥ 80	≥ 80
HDT B/ 0,45	ISO 75-2	°C	> 45	> 40
Rockwell hardness (R scale)	ISO 2039-2	-		

### Mechanical and barrier data measured on 25 micron film

			PBAT	PBST	
Tensile strength	ISO 527	MPa	TD	38	33
			MD	40	35
Elongation at Break	ISO 527	%	TD	600	650
			MD	670	700

### Valori barriera

			PBAT	PBST
Oxygen (23°C, dried)	ASTM D 3985	cm <sup>3</sup> /(m <sup>2</sup> *d*bar)	1380	1230
Water Vapor Transmission Rate (23°C, 85% r.h.)	ASTM F 1249	g/(m <sup>2</sup> *d)	165	130

## Conclusions

This article had as its objective the dissemination of knowledge, unfortunately too often lame or lame, on the panorama, on the types and technical characteristics of a series of polymers that are part of the constellation, which arouses more and more interest and debate, relating to the world of "Bio". The latter term should be used with greater attention and knowledge of the facts, especially by insiders, to avoid a series of misunderstandings on the agenda in recent years. Far from wanting to have been exhaustive in this roundup, which as indicated mainly relates to already fully industrialized polymers, we believe that this small contribution can be of support to all those, technical and non-technical, who want to approach the sector with a healthy scientific curiosity.