Succinity

BIOBASE YOUR SUCCESS

Biobased Polybutylene Succinate (PBS) –
An attractive polymer for biopolymer compounds

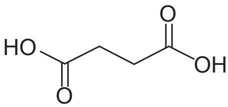
supported by

nova institute

for ecology and innovation

Polybutylene Succinate – An interesting building block for biopolymer compounds based on biobased succinic acid

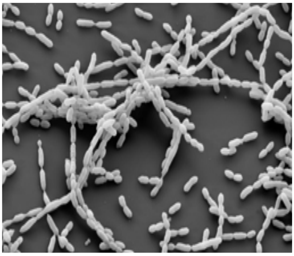
Polybutylene Succinate (PBS) is a biopolymer from poly-condensation of Succinic Acid and 1-4 Butanediol (BDO), which provides plastics producers with an interesting building block for biopolymer compounds. This brochure is targeted at providing an introduction to PBS and its building blocks and application areas.



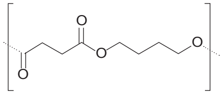
Biobased Succinic acid (BBSA) is one of the most important new chemicals of the biobased economy. It is a very versatile building block, which is expected to develop into a platform chemical with a broad range of applications, from high-value niche applications such as personal care products and food additives, to large volume applications such as bio-polyesters, polyurethanes, resins and coatings.

The U.S. Department of Energy classified it as one of the twelve most promising chemical biobased building blocks for the future. Succinic acid is a white and odorless solid that has traditionally been produced by petrochemical routes, such as the hydrogenation of maleic anhydride.

New biotechnological routes now allow the production of succinic acid based on renewable feedstocks, such as glucose, sucrose and biobased glycerol, and in the future also from second generation renewable feedstocks. The advantage of biobased succinic acid versus the conventional petrochemical route is a significant improvement of the material carbon footprint through the usage of renewable resources. Furthermore, it is expected that the new fermentative production routes allow for a more cost-competitive production of succinic acid at scale. Due to these factors, the market for succinic acid, which is small and fragmented, is expected to grow substantially from 40kt/a in 2016 by >10% CAGR over the coming years.



Renewable 1,4-butanediol (BDO from renewable resources) is a liquid, colorless, di-alcohol. Like petro-based BDO and its derivatives, BDO from renewable resources and its derivatives are valuable intermediates in a large number of applications. It is used used for producing engineering plastics, biodegradable plastics, polyurethanes and elastic fibres for the packaging, automotive, textile, and sports and leisure industries, among others. Similar to BBSA, BDO from renewable resources is produced by fermentation based on renewable feedstocks (such as dextrose) and provides an improved material carbon footprint compared to petrochemically derived BDO.



Polybutylene Succinate (PBS) is a biodegradable and compostable (according to DIN EN 13432) polyester, which is produced from succinic acid, 1,4-butanediol and eventually a third monomer which is an organic di-acid in most cases.

It was exclusively derived from fossil raw materials in the past, but can now be 100% biobased depending on the choice of monomers. PBS is expected to grow and profit from the availability and lower cost of biobased succinic acid compared to petrochemical alternatives. There are already a few producers with existing commercial capacities for the production of PBS and additional dedicated and non-dedicated capacities are expected to start up in the coming years.

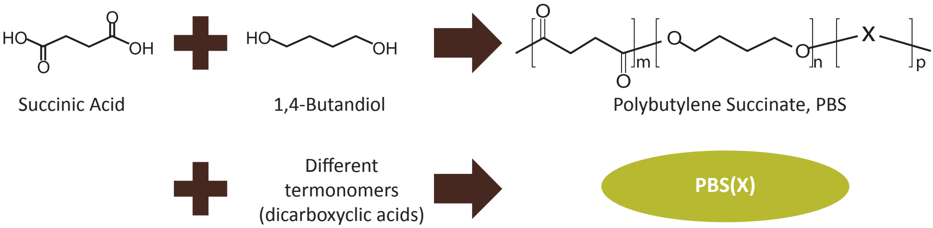
PBS is a crystalline polyester with a melting temperature exceeding 100°C, which is important for applications that require a high temperature range. Generally speaking, processing temperatures up to ca. 200°C may be used, depending on the conversion method. At those high temperatures it is crucial though that residence time is low not to decrease properties due to chain scissions, degradation and increased fluidity. An overview about the mechanical properties of PBS and PBSA, a common co-polymer of PBS containing adipic acid, in comparison with other biopolymers and common petro-based polymers is shown in table 1. Compared with standard petro-based plastics, PBS is most similar to LDPE in its properties.

Table 1: Comparison of exemplary physical properties of PBS compared to other(biobased) polymers

	PBS	PBSA	PLA	HDPE	LDPE	PS	PP
Glass Transition Temperature (Celsius)	-32	-45	55	-120	-120 - -40	105	-5
Melting Point (Celsius)	114	96	140 - 180	129	110	Amorphous	163
Heat Distortion Temperature (HDT-B, Celsius)	97	69	55	82	49	95	110
Tensile Strength (MPa)	34	19	66	28	10	46 - 60	33
Elongation at break (J/m, %)	560	807	4	700	300	3 - 4	415
Degree of Crystallinity (%)	34 - 45	20 - 30	0 - 40	69	49	0	56

Source: Xu et al., 2010

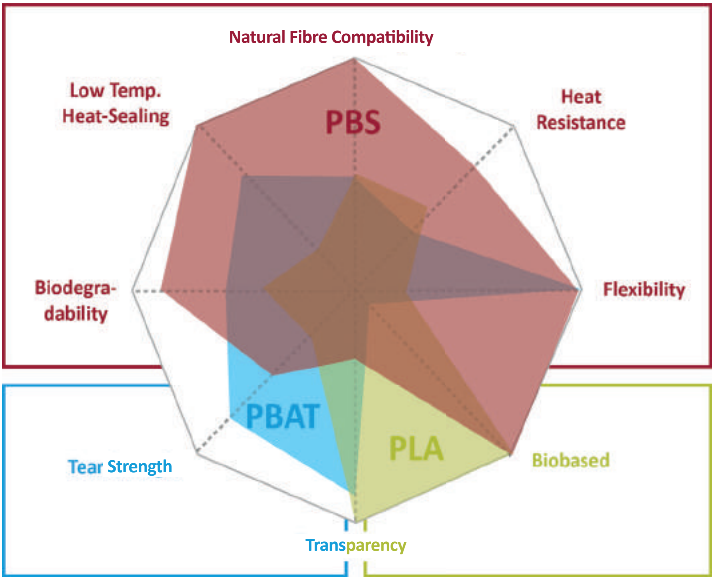
Figure 1: PBS and its production route; tailoring of properties via copolymerization



In direct comparison with PBAT and PLA (highly depending on specific grades), PBS has strengths amongst others in flexibility, natural fibre compatibility, heat resistance and biodegradability under specific conditions (according to DIN EN 13432), as shown in figure 2. PBS generally has a higher melting point and is less brittle than PLA. This combination of properties makes PBS/PLA compounds especially interesting for bioplastics producers.

PBS is usually obtained in a crystallized form and delivered in pellets. PBS has a wide processing/temperature window. PBS grades of different melt flow indices are available that are suitable for extrusion, injection moulding, thermoforming, fibre spinning and film blowing. PBS processability can be further improved by several compounding strategies while still maintaining properties regarding softness and brittleness.

Figure 2: PBS properties vs. biobased alternatives



Source: Mitsubishi Chemicals Corporation

Table 2 shows some of the PBS compounds mentioned in literature and provides some guidance on the tuning of properties.

Amongst the different possibilities for PBS copolymers, PBST and PBSA are the most commonly mentioned copolymers. Apart from these, other created copolymers include the standard PBS monomers copolymerized with benzyl succinic acid, ethylene glycol, methyl succinic acid. Generally speaking, copolymerization yields higher impact strength and elongation at break.

Figure 3: Different PBS compounds

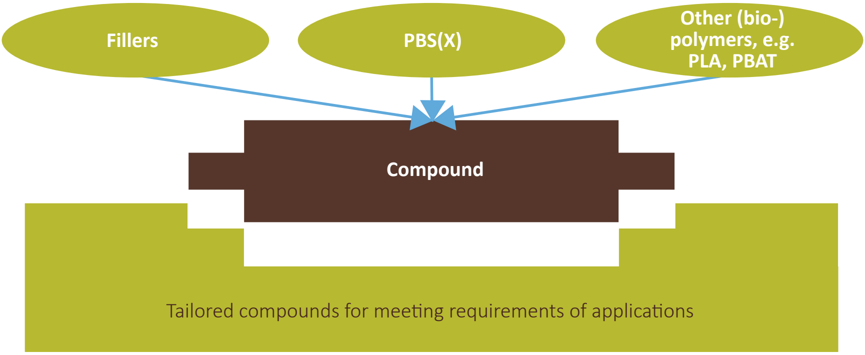


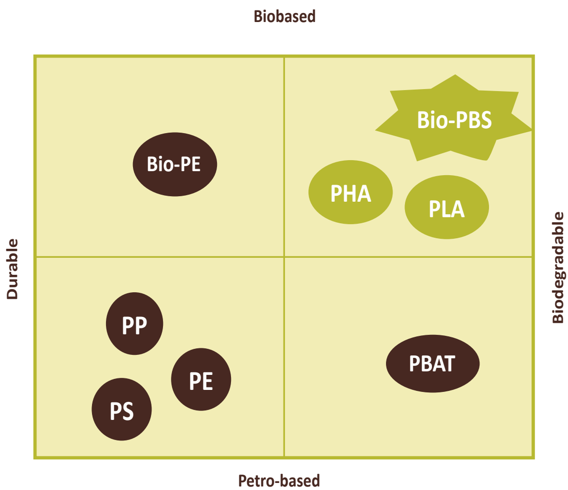
Table 2: Compunding and blending of PBS tunes various properties

PBS Compounds/Blends	Improved Properties
PBS(A)	crystallinity, tensile strength, biodegradation
PBS-PLA	tensile strength, elastic modulus, elongation at break, ductility
PBSA-PLA	impact, strength, ductility
PBS-talcum	cost, heat distortion temperature, creep resistance
PBS-PBAT	tensile strength, toughness
PBS-carbon nanotube	tensile modulus, conductivity, storage moduli
PBS-PLA-CaSO4whiskers	crystallinization, thermal resistance, impact resistance, elongation at break

Source: Illustration adapted from Ali et al., 2010; Xu et al., 2010; Ojijo et al., 2013; Chen et al., 2014; Bureepukdee et al., 2015; Muthuraj et al., 2015; Nobile et al., 2015

Sustainability of Bio-PBS

Figure 4: PBS in the bioplastics material matrix



Source: Adapted from European Bioplastics Association

Bio-PBS takes an interesting spot in the bioplastics material coordinate system due to its up to 100% biobased content and its biodegradability under industrial conditions.
The usage of biobased succinic acid and BDO from renewable resources increases the biobased content and reduces the carbon footprint of a product. First calculations show that the greenhouse gas emissions (GHG) can be reduced by ca. 50% to 80% compared to the fossil counterpart (Cok et al., 2014).

Succinic acid also has the advantage of capturing CO_2. It was estimated that per tonne of SA, 4.5 – 5 tonnes of CO_2 can be bound to the succinic acid molecule, based on literature data (Gunnarson et al., 2015).

Other screening LCAs ranging from various production processes for monomers of PBS, the polymerisation to PBS ((including formulations with additives, surface treatments for films) and mechanical/enzymatic recycling have been conducted (Succipack, 2014). Full LCA for PBS compounds is available in literature and from major producers.

Various PBS grades on the market are certified biodegradable according to EN 13432. The results of enzymatic hydrolytic as well as environmental degradation of PBS are highly depending on the environment, the composition of the PBS grade and its compound.

The "Biomass Utilization Efficiency (BUE)" is a new and relatively simple approach, developed by the nova institute, to evaluate and compare different biobased chemicals, materials and fuels based on the input-biomass, the used conversion process and the end product (Iffland et al., 2015). The BUE approach can assess which biomass in combination with a specific (bio)chemical process route is more efficient in producing different materials and evaluates which share of the biomass ends up in the product.
Biobased product pathways with a higher BUE need less land area for cultivation for the same amount of output, compared to pathways with a lower BUE. As the following table shows, PBS has a relatively high BUE compared to biobased ethylene and PE. In total 1.5 tons glucose will be needed for the production of 1 ton PBS. In contrast, 3.5 tons of glucose are needed for the production of one ton of (poly)ethylene. This means that biobased polyethylene-production needs twice the feedstock cultivation area compared to PBS.

Table 3: BUE-Comparison of SA and PBS with the drop-in chemicals ethylene and PE.

PRODUCT	STOICHIOMETRIC PERCENTAGE OF USED BIOMASS ENDING UP IN DESIRED PRODUCT	**BUE_S** In (%)	HIGHEST REALISTIC PERCENTAGE OF USED BIOMASS ENDING UP IN DESIRED PRODUCT	**BUE_H** In (%)
Succinic Acid		100.0		90.0
PBS		95.5		63.0
Ethylene		31.3		28.6
PE		31.1		28.6

Applications for PBS

PBS has various potential applications, as shown in Figure 3. Using conventional melt-processing techniques, it is possible to use PBS in electronics and other consumer goods applications as well as various (food) packaging applications such as tea cups, plates and bowls. Thanks to its biodegradability (according to DIN EN 13432) PBS can also find its way into applications where compostability is important, for instance in agricultural mulch films.

Figure 5: Overview about known possible PBS applications

PBS

Packaging/ Disposables

- Food packaging
- Coffee capsules
- Food service ware

Agriculture

- Mulch film
- Plant pots

Fibres/ Nonwovens

- Hygiene products (e.g. diapers)
- Fishing nets and lines

Industrial/ Automotive

- Wood-plastic composites
- Composites with natural fibres

Source: Adapted from Ullah et al., 2015

The packaging industry has a considerable interest in biodegradable polymers to substitute non-biodegradable polyethylene (PE), polypropylene (PP) and polystyrene plastics (PS). PBS can be used in food packaging, disposable cups and cutlery for example.




A special feature of PBS is its blendability with other plastics, including both biobased and conventional polymers; even the creation of wood plastic composites is possible. When blending PBS with PLA, its processability and mechanical properties improve. PBS compounds with PBAT or thermoplastic starch can make its use more economical. Another interesting application for PBS is in combination with PLA for 3D printing.

Summary: Unique selling points of PBS in comparison to other (biobased) chemicals (based on ecological, physico-chemical properties)

PBS is an interesting biopolymer that shows excellent biodegradability, processability and balanced mechanical properties.

- ✓ High flexibility and heat resistance.
- ✓ A wide processing window, which makes the resin suitable for extrusion, injection moulding, thermoforming, fibre spinning and film blowing.
- ✓ The physical properties and biodegradation rate of PBS materials can be tailored through composition control with different types and various contents of monomers.
- ✓ PBS can also be readily compounded with other (bio)polymers to tune the performances of the material.
- ✓ PBS shows a good binding to natural fibres without any additional bonding agent.
- ✓ Up to 100% biobased (when using BBSA and BDO from renewable resources), enabling an improved material carbon footprint compared to alternatives based on fossile resources.
- ✓ Biodegradable under industrial conditions (EN13432).
- ✓ Biobased succinic acid and PBS have a high Biomass Utilization Efficiency (BUE) compared to other biobased building blocks.

Due to these interesting material properties and compounding possibilities, PBS based on Biobased Succinic Acid can make a valuable contribution to the development of new materials as well as applications in the framework of the growing biobased economy.

6. References

Aeschelmann, F., Carus, M. et al. (2015) Biobased Building Blocks and Polymers in the World – Capacities, Production and Applications: Status Quo and Trends towards 2020. nova-Institute.

Almqvist, H. (2015). Succinic acid production from pentose rich sources in Actinobacillus succinogenes. In 37th Symposium on Biotechnology for Fuels and Chemicals. Simb.

Bautista, M., de Ilarduya, A. M., Alla, A., & Muñoz-Guerra, S. (2015). Poly (butylene succinate) Ionomers with Enhanced Hydrodegradability. Polymers, 7(7), 1232-1247.

Bozell, J. J., & Petersen, G. R. (2010). Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "top 10" revisited. Green Chemistry, 12(4), 539-554.

Brunner, C.T. (2011). „Performance of biodegradable microcapsules of poly(butylene succinate), poly(butylene succinate-co-adipate)and poly(butylene terephthalate-co-adipate) as drug encapsulation systems". Colloids and Surfaces B:Biointerfaces 84 (2): 498–507.

Cok, B., Tsiropoulos, I., Roes, A. L., & Patel, M. K. (2014). Succinic acid production derived from carbohydrates: An energy and greenhouse gas assessment of a platform chemical toward a bio-based economy. Biofuels, Bioproducts and Biorefining, 8(1), 16-29.

Duarte, J. C., Valença, G. P., Moran, P. J., & Rodrigues, J. A. R. (2015). Microbial production of Propionic and Succinic acid from Sorbitol using Propionibacterium acidipropionici. AMB Express, 5(1), 13.

Dutta, S., Wu, L., & Mascal, M. (2015). Efficient, metal-free production of succinic acid by oxidation of biomass-derived levulinic acid with hydrogen peroxide. Green Chemistry, 17(4), 2335-2338.

Fujimaki, T. (1998). „Processability and properties of aliphatic polyesters, ‚BIONOLLE', synthesized by polycondensation reaction". Polymer Degradation and Stability 29 (1-3): 209–214.

Gunnarsson, I. B., Kuglarz, M., Karakashev, D., & Angelidaki, I. (2015). Thermochemical pretreatments for enhancing succinic acid production from industrial hemp (Cannabis sativa L.). Bioresource technology, 182, 58-66.

Gunnarsson PhD thesis 2015; Bai, B., Zhou, J. M., Yang, M. H., Liu, Y. L., Xu, X. H., & Xing, J. M. (2015). Efficient production of succinic acid from macroalgae hydrolysate by metabolically engineered Escherichia coli. Bioresource technology, 185, 56-61.

Hong, C. M., Wang, X. J., Kong, P., Pan, Z. G., & Wang, X. Y. (2015). Effect of succinic acid on the shrinkage of unsaturated polyester resin. Journal of Applied Polymer Science, 132(2).

Iffland, K., Sherwood, J., Carus M., Raschka, A., Farmer, T., Clark, J. (2015). Definition, Calculation and Comparison of the "Biomass Utilization Efficiency (BUE)" of Various Bio-based Chemicals, Polymers and Fuels, Hürth 2015-11.

Jacquel, N (2011). „Synthesis and properties of poly (butylene succinate): Efficiency of different transesterification catalysts". J. Polym. Sci., Part A: Polym. Chem 49 (24): 5301–5312.

Kamzolova, S. V., Vinokurova, N. G., Dedyukhina, E. G., Samoilenko, V. A., Lunina, J. N., Mironov, A. A., and Morgunov, I. G. (2014). The peculiarities of succinic acid production from rapeseed oil by Yarrowia lipolytica yeast. Applied microbiology and biotechnology, 98(9), 4149-4157.

Kongruang, S., & Kangsadan, T. (2015). Optimization of Succinic Acid Production from Crude Glycerol by Encapsulated Anaerobiospirillum succinicproducens Using Response Surface Methodology. International Journal of Bioscience, Biochemistry and Bioinformatics, 5(1), 11.
Li, L., Qu, W., Zhang, X., Lu, J., Chen, R., Wu, F., & Amine, K. (2015). Succinic acid-based leaching system: A sustainable process for recovery of valuable metals from spent Li-ion batteries. Journal of Power Sources, 282, 544-551.

Lin, C. S., Luque, R., Clark, J. H., Webb, C., & Du, C. (2011). A seawater-based biorefining strategy for fermentative production and chemical transformations of succinic acid. Energy & Environmental Science, 4(4), 1471-1479.

Lu, C. D., Xiong, Y. Y., Zhao, J. F., & Wang, J. H. (2015, March). Fermentation Production of Succinic Acid from Sucrose by Engineered Escherichia Coli JH208. In Advanced Materials Research (Vol. 1088, pp. 503-506).

Luque, R., Clark, J. H., Webb, C., & Du, C. (2012). Wheat-based biorefining strategy for fermentative production and chemical transformations of succinic acid. Biofuels, Bioproducts and Biorefining, 6(1), 88-104.

Succipack consortium (2014). FP7 project on active, intelligent and sustainable food packaging using polybutylene succinate. http://www.succipack.eu/docs/pdf/pdf1%20Final%20report.pdf

Sun, Z., Li, M., Qi, Q., Gao, C., & Lin, C. S. K. (2014). Mixed food waste as renewable feedstock in succinic acid fermentation. Applied biochemistry and biotechnology, 174(5), 1822-1833.

van Heerden, C.D.; Nicol, W. (2013). "Continuous and batch cultures of Escherichia coli KJ134 for succinic acid fermentation: metabolic flux distributions and production characteristics", Microbial Cell Factories, 12:80

van Heerden, C.D.; Nicol, W. (2013). „Continuous succinic acid fermentation by Actinobacillus succinogenes". Biochemical Engineering Journal, 73.

Wang, C., Thygesen, A., Liu, Y., Li, Q., Yang, M., Dang, D., ... & Xing, J. (2013). Bio-oil based biorefinery strategy for the production of succinic acid. Biotechnology for biofuels, 6(1), 1-10.

Xu, J. (2010). „Microbial Succinic acid, its polymer poly(butylene succinate), and applications". Plastics from bateria: 347–388.

Xu, J., & Guo, B. H. (2010). Poly (butylene succinate) and its copolymers: research, development and industrialization. Biotechnology Journal, 5(11), 1149-1163.

Yutaka, T., Buenaventurada, P. C., Ugwu, C. and Aiba, S. (2009). Biodegradability of Plastics International Journal of Molecular Science 9: 3722–3742.

Zeikus, J. G., Jain, M. K., & Elankovan, P. (1999). Biotechnology of succinic acid production and markets for derived industrial products. Applied Microbiology and Biotechnology, 51(5), 545-552.

SUCCINITY GMBH
A joint venture of BASF and Corbion

Schirmerstr. 80
40211 Düsseldorf
Germany

Phone: +49 211 989138-0
info@succinity.com
www.succinity.com

NOVA-INSTITUTE

Chemiepark Knapsack
Industriestr. 300
Gebäude 0611
50354 Hürth

Phone: +49 2233 48 14 40
contact@nova-institut.de
www.nova-institut.eu