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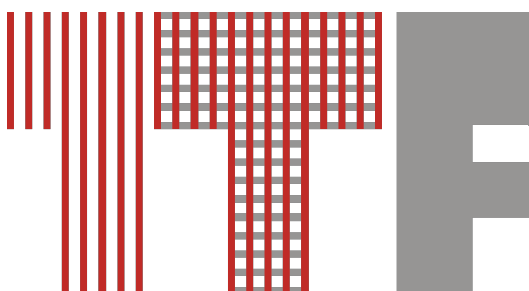
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Bioplastics in Textiles*

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Abstract

Large quantities of available biomass that needs to be used are the main reason for bioplastics revival. In many cases it is an optimal solution for a particular purpose. The production of textile used for clothing, medicine, and the automotive industry being the main consumer of technical textile where textile constitutes almost 85% of the car interior follow this trend. The important reasons for application are functionality and biomass utilization. Permanent increase in bioplastic production capacity is expected. The paper presents new achievements in textiles and the related areas.

KEY WORDS:

bioplastics
environment
polymers
textile

KLJUČNE RIJEČI:

bioplastika
okoliš
polimeri
tekstil

Bioplastika u tekstilu

Sažetak

Zbog velike količine raspoložive biomase koju treba iskoristiti bioplastika doživljava renesansu. U nekim je slučajevima dobro rješenje za određenu namjenu. Takav trend slijedi i proizvodnja tekstila za potrebe odijevanja, medicine i automobilske industrije, glavnoga korisnika tehničkog tekstila, gdje tekstil čini gotovo 85 % unutrašnjosti automobila. Važni razlozi primjene su funkcionalnost i iskoristivost otpadne biomase te se očekuje trajno povećanje kapaciteta za proizvodnju bioplastike. U radu su prikazana nova dostignuća u tekstilstvu i srodnim granama.

Introduction

Manufacturers accept bioplastics for numerous reasons, mainly because of the belief in climate changes, highly variable prices of petroleum and natural gas, the main feedstock for synthetic plastic production (fossil plastics). The first plastics were made by using biomaterials, such as cellulose, casein or soy. These materials were partially forgotten after

the possibility of obtaining plastics from petroleum and natural gas was discovered. However, the important reasons for bioplastic applications today are their functionality and biomass usability. As material, bioplastics can be used for textile products: clothes and shoes, sport's bags and equipment, some medical devices, and automotive parts.¹⁻⁶

Despite high efforts of the leading world's bioplastic manufacturers, its share in the total plastic consumption in 2011 was less than 0.5%. A permanent increase in bioplastic production capacity is expected, but in foreseeable future its share will not be at a level higher than few percentages of the total plastic production.⁷

The materials primarily used for textile in the near future are the following: polylactides (PLA), poly(hydroxy-alkanoates) (PHA), poly(hydroxy-butyrate) (PHB), poly(glycolide) (PGA) and its blends, bio-polyester (bio-PES), bio-polyamide (bio-PA), thermoplastics based on casein (milk protein) and planted products: soy, kenaf, jute, silk, etc. (Figure 1).

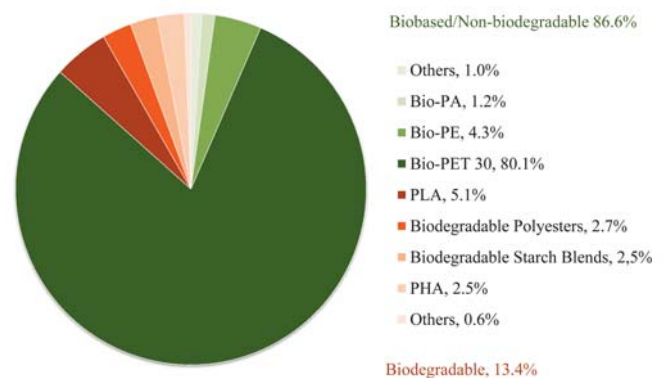


FIGURE 1 – Global bioplastic production capacity prediction for the year 2016⁸

Bioplastics for textile industry needs

According to the *European Bioplastics*, bioplastics are plastics derived mostly from renewable biomass including polymers that meet the standards for biodegradability and compostability (EN 13432 / EN 14995).⁸⁻⁹

Certain materials used in the textile industry nowadays or that will be used in the near future will be briefly described in the following section of this paper.

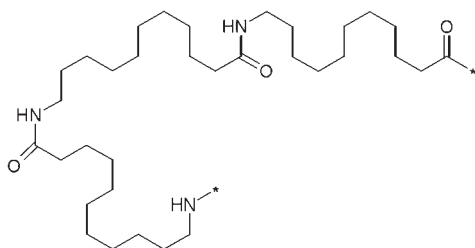
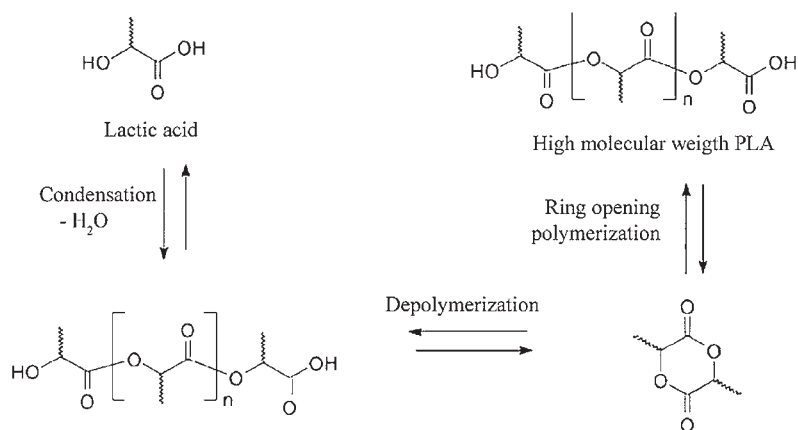
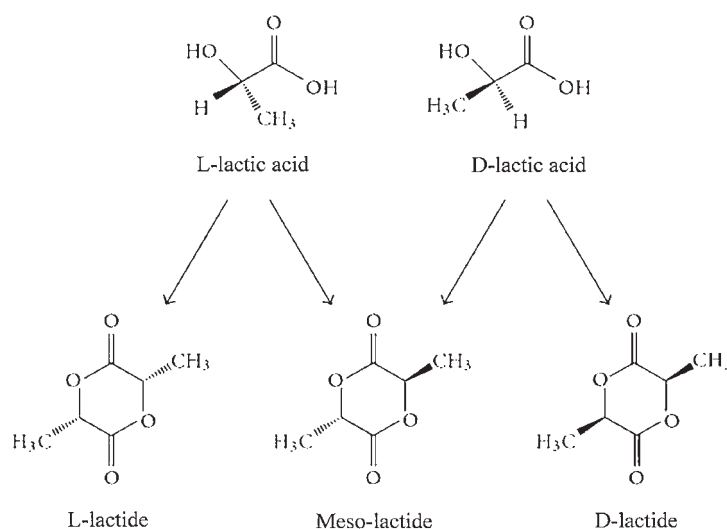
Polyamides

Polyamide 11, PA 11 (Figure 2) is produced from castor oil and is not biodegradable. It is resistant to water and hydrocarbons, provides good thermal and mechanical properties.²

Poly lactides

Poly lactides, PLA, are produced from corn and sugar beet.¹¹⁻¹⁴ Despite the fact that PLA realize good balance between the properties of bioplastics and environmental advantages compared to many synthetic plastics its production costs are still too high. Poly lactides can be produced by direct condensation of lactic acid or by ring-opening polymerization (Figure 3).¹²

* This work is based on the paper presented at the Conference *Bioplastics*, Society of Plastics and Rubber Engineers, Zagreb, 22nd November, 2012.

FIGURE 2 – Polyamide 11¹⁰FIGURE 3 – Schematic view of PLA production¹²FIGURE 4 – Lactide types¹⁴

Current industrial lactic acid production is based on microbial fermentation of carbohydrates and enables the optically pure lactic acid production. The optical purity of lactic acid reagent is crucial during PLA manufacture: even small amounts of enantiomeric impurities can significantly change the properties of PLA, such as crystallinity or biodegradation rate.¹¹⁻¹⁴ There are three different PLA types: L,L-lactide, D,D-lactide, and D,L-lactide (Figure 4). From these PLA types; PDLA and PLLA are particularly interesting for the textile industry and production of diapers, textiles and hygiene products usually in combination with cotton.¹⁴⁻¹⁷

Poly(glycolide)

Poly(glycolide), PGA, is a biodegradable bioplastic and can be used in medical textile area.¹⁸⁻¹⁹ The PGA polymerization reaction is shown in Figure 5. Poly(glycolide) is highly crystalline (45 - 55%) with high melting point between 220 - 225°C and glass transition temperature of 35 - 40°C. Because of its high degree of crystallization, it is not soluble in most organic solvents. Fibres from PGA exhibit high strength and modulus and are too stiff to be used as sutures except as braided material. Therefore, PGA is used in medicine as sutures, which lose about 50% of their strength after two weeks, 100% after four weeks and are completely absorbed in 4 - 6 months (healthy immune system, normal body temperature up to 37°C, etc.).²⁰

Poly(hydroxy-alkanoates)

Poly(hydroxy-alkanoates), PHAs (Figure 6), are biodegradable bioplastics of high molecular weight which are included in thermoplastics. Microbial production of PHAs is possible by bacteria *Alcaligenes eutrophus*, *Alcaligenes latus* and *Pseudomonas oleovorans*, and by using carbon sources of glucose, fructose and sucrose (Figure 7). From the textile point of view, PHAs are used for medical products.²⁰

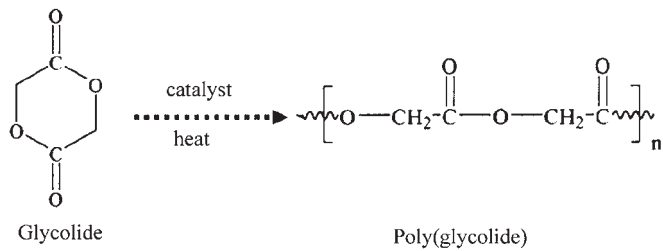


FIGURE 5 – PGA synthesis²⁰

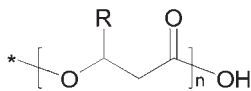


FIGURE 6 – General PHAs chemical structure²¹

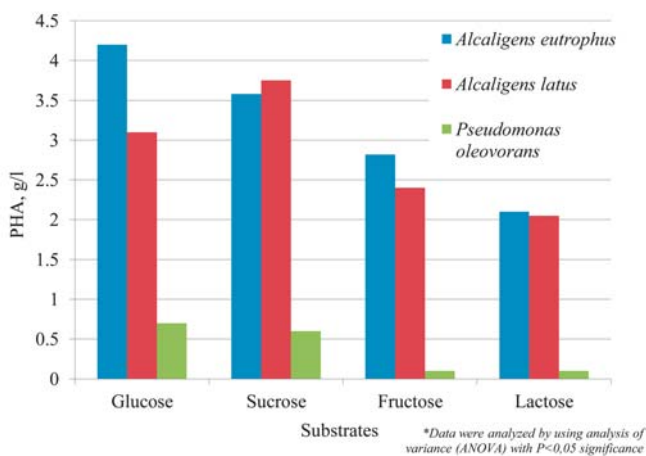


FIGURE 7 – Comparative data of PHAs production by *Alcaligenes eutrophus*, *Alcaligenes latus* and *Pseudomonas oleovorans* with various carbon sources²²

Poly(hydroxy-butyrat)

Poly(hydroxy-butyrat), PHB (Figure 8)²³, is biodegradable bioplastics produced mostly from starch of potato, wheat, corn. According to recent studies, the action of bacteria *Bacillus mycoides* results in a large PHB amount from wheat starch (Table 1).²⁴ PHB production can be obtained from *Jawar* stem, waste product after harvesting *Jawar* crop (*Sorghum bicolor*); *Neera* natural drink extracted from inflorescence of Toddy plant (*Borassus flabellifer*); sugarcane bagasse; coconut pulp (Table 2).²⁵ Main PHB applications are present in pharmaceutical industry, development of medical sutures, bone marrow scaffolds, tissue engineering.²

TABLE 1 – PHB production by *Bacillus mycoides*²⁴

Carbon source	Cell dry weight, g/l	PHB, g/l	PHB content, %
Potato starch	0.638 ± 0.3	0.058 ± 0.66	9.09 ± 0.47
Wheat starch	3.89 ± 0.6	1.28 ± 0.34	33.05 ± 0.58
Corn starch	3.45 ± 0.4	0.486 ± 0.52	14.08 ± 0.65

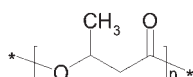


FIGURE 8 – PHB chemical structure²³

TABLE 2 – PHB production by *Bacillus* species²⁵

Agroindustrial source	Sugar concentration, mg/ml	Microorganism	Cell biomass (dry weight), mg/l	*PHB, mg/l
<i>Jawar</i> stem	1.90	<i>Bacillus subtilis</i>	8.56	0.034
		<i>Bacillus cereus</i>	6.72	0.049
<i>Neera</i> plant	2.52	<i>Bacillus subtilis</i>	6.440	0.284
		<i>Bacillus cereus</i>	4.448	0.152
Bagasse	3.17	<i>Bacillus megaterium</i>	2.257	0.199
Coconut pulp	2.01		2.058	0.079

* Dry PHB weight / dry cell biomass

Thermoplastics based on milk proteins for biofibres

New materials for biofibre production are thermoplastics based on milk proteins. In Germany two million tons of milk are thrown away due to very strict food requirements. Bremen Fibre Institute manufactures *Qmilch* thermoplastic biofibres using disposable milk. The fibres are spun from casein (Figure 9), obtained from dry milk powder, water, and other natural substances such as beeswax using a device similar to an extruder. Fibres can be fine or coarse, filament or staple depending on the application (Figure 10).²⁶⁻³¹

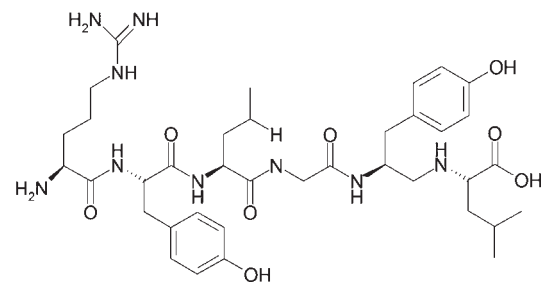


FIGURE 9 – α-casein (90-95)³²

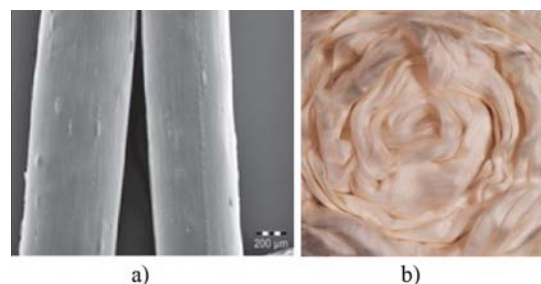


FIGURE 10 – *Qmilch*, Bremen Fibre Institute, Germany: a - Scanning electron microscope (SEM) image, b - yarn^{27,30}

Bioplastics for textile industry needs - applications

Bioplastics are used for home textiles, clothing and footwear industry, etc.

Raincoat, named *Rain Poncho*, a product of the Spanish company *Equilicua*, is an appropriate example of bioplastic protective clothing produced from potato starch (Figure 11a, b, c). This poncho is non-toxic,

cannot pollute the environment, it is 100% compostable and biodegradable. The information printed on *Rain Poncho* shows users the benefits of bioplastics, biodegradable materials and composting. In addition, seeds used for plants, flowers, trees and Mediterranean plants are embedded in poncho. The seeds are encased in small clay balls which contain nutrients that can prevent seeds from becoming bird food and protect them until they are ready for growth. This procedure is called *Nendo Dango*.^{33,34}

French company *Lacoste* has developed a protective bicycle helmet, made of wool (outer part), a special kind of bioplastic material for helmet armour, and cork as the inner layer (Figure 11d).³⁵



FIGURE 11 – Bioplastics in protective textile industry and for luggage production: a – *Rain Poncho* by *Equilicua*, b – Information printed on the *Rain Poncho*, c – *Rain Poncho* packages, d – *Lacoste* helmet concept, e – *Rilsan* ski socks by *Monnet*, f – *Rilsan* travel luggage by *Unitika*³³⁻³⁶

Polyamide 11, trade name *Rilsan*, can be used for sport socks and luggage (Figure 11e, f). Ski socks are usually very soft to the touch, lightweight, comfortable and provide good bacteriostatic and thermo-regulating properties. The outstanding characteristics of bags and luggage are high material strength and wear resistance.³⁶

Bioplastics play an important role in home textiles; there is an emphasis on quality and product functionality besides product design (Figure 12a, b).



FIGURE 12 – Bioplastics in home and fashion industry: a – Lamp by *Philippe Starck*, b – Sofa by *Teijin*, c – *Biofront* - silk kimono material by *Teijin*, d – *Qmilch* dresses by *Anke Domaske*^{8,28,39,41}

Biofront is heat resistant stereo-complex PLA bioplastics (L- and D-lactide blends, 50/50) produced by the Japanese company *Teijin* with the melting point of 210°C. *Teijin* combines this bioplastics with traditional silk for innovative products such as kimono materials which contain the texture and sheen (Figure 12c). It can be used for car seats (for example, *Mazda Motor Corporation*); car front panels and eyeglass frames.³⁷⁻⁴⁰

Thermoplastic fibres based on milk proteins are colourless, environmentally friendly, biodegradable, have antibacterial and anti-allergic properties. Textile products are washable at 60°C, regulate blood circulation and body temperature. Clothes made of these fibres are functional and comfortable to wear. Six litres of milk are needed to produce one *Qmilch* dress (Figure 12d). It can be suitable for a wide range of products - home textiles, sheets and towels, daily garments, T-shirts, socks and underwear. In addition, the automotive industry is also looking for allergen-free and sustainable materials, and these fibres can be used for car seats.²⁶⁻²⁸

The Spanish company *One Moment* produces biodegradable eco-friendly bioplastic shoes developed from high-tech materials with extremely innovative production techniques, giving the product high resistance level and elasticity (Figure 13a). Polymer injection technique allows obtaining 1 mm thickness for the shoe body, and 2 mm for the sole, at least 3 mm less than the traditional shoe. This enables higher comfort and correct skin breathing at the same time. Shoes biodegrade approximately in six months and after that can compost.⁴²



FIGURE 13 – New biodegradable bioplastic shoes: a – *One Moment* (01M) shoes, b – *Ballerina* by *Gucci*, c – Men sneakers by *Gucci*^{42,44}

The Italian company *Gucci* developed special environmentally friendly men's and women's shoes both made from bioplastics, a biodegradable material sourced from compost (the company did not indicate the type of bioplastics). *Ballerina* flats are made entirely of bioplastics (Figure 13b), while men sneakers have bio-rubber soles with a calfskin upper part, biologically certified strings, and rhodium-plated metal detailing (Figure 13c).^{43,44}

The German company *Puma* started to produce biodegradable bioplastic sneakers and shirts (Figure 14) by using biodegradable polymers, biopolyesters and organic cotton. The upper part of *Puma*'s sneaker *Basket* is made of cotton and linen blends, while the sole is composed of bioplastic *APINAT Bio*. This plastic (Italian company *Api Spa*) includes different bioplastic types from synthetic materials with renewable content of up to around 60%.^{44,45}



FIGURE 14 – Bioplastic sport textile produced by *Puma*: a – T-shirt, b – Sneakers, c – Lifecycle of sneakers⁴⁵

The automotive industry is the major user of technical textiles, and bioplastics have an important influence on the production of car interiors,

car seats and other parts.⁴⁶ An average car, weighing 1,500 kg, contains 14-20 kg of textiles and textile components. According to research activities the amount of textile components will grow to 35 kg until 2020.⁴⁶⁻⁵² Road transport is the second largest source of greenhouse gas emissions in the EU and with new legislation the emissions will be reduced by 10% between 2010 and 2020. One of the legislation guidelines is to increase the usage of textile components inside vehicles, which are easily maintained and recycled at the end of their lifecycle. The key factors are manufacturing costs and material weight.⁵⁰ In 2003 Ford researchers first showed that soybean oil derivatives are useful for the automotive industry. The end product can be foam used for products such as car seats, vehicle cushions, armrests and headrests, etc. Ford started to use wheat straw for certain car parts as well (Figure 15).⁵¹⁻⁵²



FIGURE 15 – Bioplastics made from wheat straw and polypropylene⁵¹

The development of biocomposites based on different bioplastic polymer types (PLA, PHB) reinforced with fibres from plant products (kenaf, flax, sisal) was made possible. In these fibre reinforced composites - the fibres serve as reinforcement by giving strength and stiffness to the composite structure while the polymer matrix holds the fibres together. Such composites are lightweight and have high strength. The modulus of elasticity and tensile strength are increased with increasing the fibre content in composites. Fibre reinforced biocomposites provide significantly better thermal and sound insulations in cars than glass fibre reinforced composites, reduce irritation to skin and respiratory system.^{50,54} Vehicles in some BMW series contain up to 24 kg of flax and sisal.⁵³ The results show that kenaf fibre reinforced biocomposites have good mechanical properties, high strength and stiffness. In the future, biocomposites with long decomposition time can be good replacement in the automotive industry as construction materials.^{50,54}

Bioplastics is important in medical textiles, especially the PLA, for the production of surgical gloves and protective suits; it can significantly reduce medical waste. It is not necessary to remove surgical threads made of PLA; their degradation occurs after a while.² Tissue engineering is a part of the regenerative medicine which aims at replacing or rebuilding the tissue or organ due to disease, trauma, or aging. Creating tissue for medical appliance is used in hospitals for various applications, such as skin, mucous membranes, bones, ligaments, etc. Scaffolding must possess adequate mechanical properties, should be porous, permeable, allow the entry of cells and nutrients, and show appropriate surface structure.^{18, 55, 56}

In implant preparation the human cells taken from certain organs are grown on textile backbone in 2-D/3-D shape. The skeleton, i.e. textile base, is made of fibres obtained from compatible and degradable poly-

mers. The best known fibres for this purpose are PLA and PGA fibres, which can be used as individual polymers or co-polymers of PLA/PGA. During degradation fibrous connective tissue replaces the implant that slowly breaks down in the body (no further surgery needed, patient recovery is faster). Furthermore, meshes produced from PGA fibres (Figure 16a) are completely degraded after implantation in the body within 90 days. Current bioplastic innovations are the development of narrow tubular guides made of PGA yarns, which are used in the reconstruction of peripheral severed nerves of hands (Figure 16b).¹¹

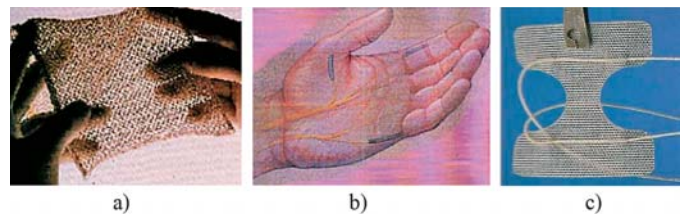


FIGURE 16 – Medical textile: a – mesh, b – nerves, c – membrane^{11, 57}

Biodegradable PLA/PLGA microporous membrane (Figure 16c) can be used to regenerate defective periodontal tissue, shows appropriate bandwidth of nutrients, safety and therapeutic efficiency. It retains its integrity for 6 to 8 weeks, which is enough to maintain the space in periodontal pocket.^{20,55,57}

Conclusion

Bioplastics are the subject of numerous studies and have been increasingly present in the world today. Their applications are rapidly growing in all fields of human activities. Some manufacturers in the automotive industry play a leading role in bioplastic usage (Ford, BMW). Europe is the most interesting market, but the production has also expanded in Asia and South America. Products based on biomass, especially in textile and related industries, are very promising. Currently, the bioplastic production cost is one of the major factors that determine the effectiveness of their implementation. It is expected that bioplastics will become cheaper, particularly as consequence of the development of new technologies and by achieving the required economy.

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