

Polymers Based on Renewable Raw Materials – Part II

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S. Jovanović,^{a*} J. V. Džunuzović,^b and Ž. Stojanović^c

^a Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11 120 Belgrade, Serbia

^b Institute of Chemistry, Technology and Metallurgy (ICTM) – Center of Chemistry, University of Belgrade, Studentski trg 12–16, 11 000 Belgrade, Serbia

^c Henkel Serbia, AG General Industry, Henkel Adhesive Technologies, Bulevar Oslobođenja 383, 11 040 Belgrade, Serbia

A short review of biopolymers based on starch (starch derivatives, thermoplastic starch), lignin and hemicelluloses, chitin (chitosan) and products obtained by degradation of starch and other polysaccharides and sugars (poly(lactic acid), poly(hydroxyalkanoates)), as well as some of their basic properties and application area, are given in this part. The problem of environmental and economic feasibility of biopolymers based on renewable raw materials and their competitiveness with polymers based on fossil raw materials is discussed. Also pointed out are the problems that appear due to the increasing use of agricultural land for the production of raw materials for the chemical industry and energy, instead for the production of food for humans and animals. The optimistic assessments of experts considering the development perspectives of biopolymers based on renewable raw materials in the next ten years have also been pointed out.

At the end of the paper, the success of a team of researchers gathered around the experts from the company Bayer is indicated. They were the first in the world to develop a catalyst by which they managed to effectively activate CO₂ and incorporate it into polyols, used for the synthesis of polyurethanes in semi-industrial scale. By applying this process, for the first time a pollutant will be used as a basic raw material for the synthesis of organic compounds, which will have significant consequences on the development of the chemical industry, and therefore the production of polymers.

Key words: *Biopolymers, renewable raw materials, properties, application*

Introduction

Raw materials containing carbon are essential to the chemical industry for the production of organic substances. In the past fifty years, this demand was fulfilled mostly by fossil raw materials (oil, natural gas and coal), while only developed countries used around 10 % of renewable raw materials of plant and animal origin.

The constantly growing prices of fossil raw materials, particularly of oil and natural gas, as well as the harmful effects of their use on the environment have prompted growing interest in the use of renewable raw materials of plant and animal origin for the production of polymers and other chemicals. Literature describes numerous natural macromolecular substances – renewable raw materials, which may be transformed directly or after appropriate physical, chemical or biochemical modifications into biodegradable or non-biodegradable polymers and low molecular weight chemicals.

Apart from being used for the production of food for humans and animals, as well as chemicals and polymers in

the chemical industry, renewable raw materials, *i.e.* biomass, is increasingly being used for the production of energy. Because of the competition in the use of agricultural land, a significant increase in food prices has occurred. Taking into account the rapid growth of the global population, and the associated need to increase food production, researchers around the world have already started to question the thesis that the amount of biomass produced per year is sufficient to meet the needs of producers of food, chemical products and energy, and whether it is possible in the foreseeable future to completely replace fossil raw materials in the chemical industry with renewable raw materials. Bearing in mind that the use of renewable raw materials for the production of polymeric materials is economically and environmentally the most acceptable, due to their possible reuse and recycling, it is expected that their production from renewable raw materials will prevail compared to the production of energy, especially as there are other alternative procedures for energy production.

Part I of this paper indicates the basic definitions of biopolymers, the raw materials for their production, as well as describes their application areas, existing production capacities, and the properties of cellulose from wood and annual plants, as the most important renewable raw ma-

* Corresponding author: Prof. dr. Slobodan Jovanović
e-mail: bobajov@open.telekom.rs

material for the chemical industry.¹ Part II describes only selected examples of renewable raw materials and biodegradable polymers based on these raw materials, which already have their place in the market of polymer materials or have a realistic chance of finding a place in the market in the near future. The environmental and economic feasibility of the application of biodegradable polymers, and the impact of using biomass for biopolymer production on food production are discussed, as well as the perspectives of production development and application of biodegradable biopolymers based on renewable raw materials.

The most commonly used biopolymers based on renewable raw materials

Starch and starch derivatives

Green plants such as potato, maize (corn), rice, and cassava are raw materials for production of biopolymers. The main component of these plants is starch. Starch is considered a potential polymer to be used in biodegradable materials because of its low cost, availability, and because it is produced from renewable resources. Since it is not a thermoplastic material, it has been used to produce blends with non-biodegradable polymers, biodegradable materials, and in injection molding.²

Starch is a mixture of two D-glucan homopolymers, composed of α -D-glucopyranosyl units (AGU), namely, amylose and amylopectin (Fig. 1). These two parts of starch have a different degree of branching. Amylose is essentially a linear polymer consisting of AGU, although some (1-6)-linkages are thought to exist at about every 180–400 units.² Amylopectin is a highly branched form of amylose, consisting of (1-4)-linked AGU and a significant portion of 1,4,6-tri-O-substituted residues acting as (1-6)-linkage branch points. Amylose and amylopectin are uniformly distributed inside the granule. Amylose constitutes amorphous region and amylopectin constitutes crystalline region.

Molecular weight of amylose depends on the starch origin. Generally, amylose extracted from cereals (degree of polymerisation, DP , of about 1000) has lower molecular weight than others (DP of about 3300). Molecular weight of amylose is connected with the degree of branching: cereal amylose has 3–5 branches per macromolecule, and amylose from sweet potato has about 10 branches per macro-

molecule.² Amylopectin is a hyperbranched component of starch. Average DP of the branches depends on the starch type, and range from 19 to 31. Molecular weight of amylopectin is much higher than that of amylose, and has a value of about 50 to 500 million, making it one of the biggest macromolecules.

The amylose/amylopectin ratio varies depending on the source of the starch and its maturity. Starch isolated from granules contains 20 – 30 % of amylose and 70 – 80 % of amylopectin. Some cultivated plant varieties have pure amylopectin starch without amylose, known as waxy starches. Waxy starches have less retrogradation, resulting in a more stable paste. High amylose starch (amylomaize) is cultivated for use because of its gel strength, and as a resistant starch (a starch that resists digestion) in food products. Beside amylose and amylopectin, there are different quantities of lipids, proteins, phosphates, etc. in granules.

In the plants, starch is organised in discrete particles – granules, whose size, shape, morphology, composition and supramolecular structure depend on the botanical source. The diameters of the granules generally range from less than 1 μm to more than 100 μm , and shapes can be regular (e.g., spherical, ovoid, or angular) or quite irregular.²

Today, the main commercially refined starches are cornflour, tapioca, wheat and potato starch. Worldwide, dry starch production amounts to about 67 million tons.³ Current annual production of primary starch sources is estimated to be 46.1 million tons of maize, 9.1 million tons of cassava, 5.15 million tons of wheat, and 2.45 million tons of potato. Starch and its derivatives are utilised in several industrial applications due to their low cost, availability, and ability to impart a broad range of functional properties to food and nonfood products.

In nonfood applications, the most traditional use of starch has been in the paper industry (about 10 million tons per year). Recently, with the increasing cost of cellulose pulp, paper producers have begun to seek lower-cost fillers. These fillers often require specially modified starches to bind them to the pulp. In addition to the use of starches in the paper and textile industries and for production of new biodegradable materials, starches can also be used in the fuel market. With new trends in the biofuel and bioethanol market, there has been increasing interest in some starchy crops.

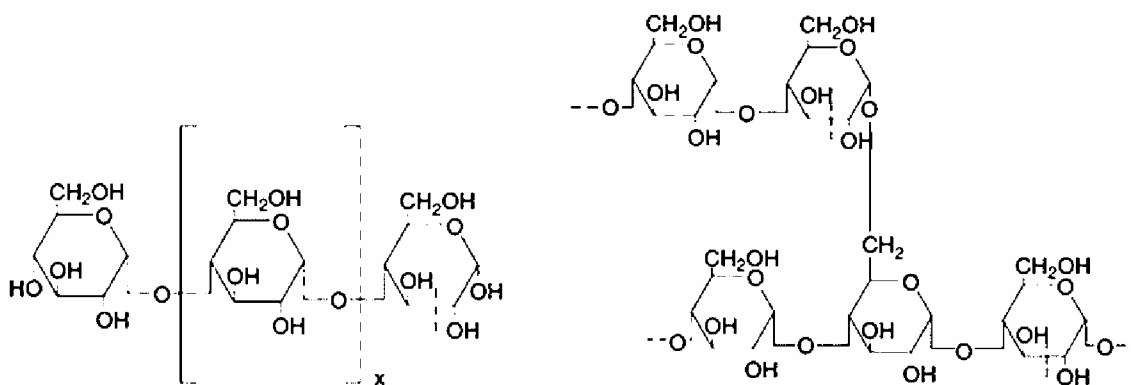


Fig. 1 – Schematic diagram of amylose (left) and amylopectin (right) with a branch point at the O6 position
Slika 1 – Shematski dijagram amiloze (lijevo) i amilopektina (desno) s grananjem u položaju O6

Modification of starch

Starches are modified chemically or physically or both to accentuate their positive characteristics, diminish their undesirable qualities or add new attributes. Common limitations associated with native normal starches are excessive viscosity at low solids content (difficulty in handling, lack of body), high susceptibility to retrogradation (gel opacity, syneresis, and lack of freeze–thaw stability) and lack of process tolerance.

Chemical modification

Chemical modification, which is the most common industrial means of enhancing starch properties, requires reaction or treatment of starch with chemical reagents to introduce new chemical substituent groups, to influence the molecular scission or promote oxidation or molecular rearrangements. Chemical modification of starch is based upon hydroxyl group chemistry and a modified starch can be defined as one whose hydroxyl groups have been altered by chemical reaction (e.g., by oxidation, esterification, etherification, crosslinking, etc.). The physicochemical properties of such modified starch are largely dependent on the degree of substitution (*DS*), which is defined as the average number of substituted hydroxyl groups per AGU. The maximum *DS* value for a single AGU is 3. Obviously, this value is reduced in the case of amylopectin, since a branched AGU has a maximum theoretical *DS* value of 2.

Products that are partially depolymerised are called “converted starches”. There are three basic processes for making converted starches:

- using acid,
- using an oxidant in an alkaline system, and
- by application of heat.

Acid-modified starches are obtained by adding a mineral acid (hydrochloric or sulphuric) in stirred slurry of starch granules at temperature below the gelatinization temperature of the starch. Oxidised starches are often produced by treatment of starch with:

- a solution of sodium hypochlorite with introducing carbonyl groups or
- hydrogen peroxide and copper(II) ions without introducing carbonyl groups or
- ammonium persulphate to depolymerise starches oxidatively for paper sizing and coating processes.

Ethers and esters of starch are produced by reacting starches with monofunctional reagents. Both esters and ethers are made in the same general way, using two-step reactions. The first step represents the activation of starch. In the past, organic solvent was used as reaction medium, while activator was pyridine or similar nucleophile. Recently, water and/or alcohol have been used as reaction medium and hydroxide as activator. An alkaline pH converts some hydroxyl groups into alkoxide ions for participation in nucleophilic substitution reactions.^{4,5}

Manufactured monostarch ethers include hydroxyethyl, hydroxypropyl, carboxymethyl, and cationic starches. Reaction with ethylene oxide produces hydroxyethyl starch,

reaction with propylene oxide produces hydroxypropyl derivatives⁶, and reaction with sodium monochloroacetate produces sodium carboxymethyl starch.⁴ The products generally have the same properties as the monosubstituted starch esters, the difference being that ethers are stable to acids and bases whereas esters are not.

As implied, cationization imparts a positive charge to the starch chains via derivatisation with reagents containing imino, amino, ammonium, sulphonium or phosphonium moieties. From a commercial perspective, the most industrially significant and commonly utilised reagent is (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTMA).^{7–9} Cationic starch derivatives are typically employed as wet end and surface sizing and coating additives in the paper industry for enhancement of sheet strength and retention of fines, as well as industrial flocculants in sludge dewatering and mineral mining operations.¹⁰ Values of *DS* for cationic starch derivatives in paper-making applications generally range from 0.02 to 0.07, while those for flocculent applications are significantly higher (*DS* \approx 0.2 – 0.7). Cationic starches are very efficient flocculants for removal of Hg^{2+} , Cu^{2+} and Zn^{2+} , with those cationic derivatives possessing primary amino groups exhibiting the highest sorption efficiency

Starch crosslinking reactions are employed to strengthen the structure of swollen granules upon gelatinisation, enhancing the resistance to viscosity breakdown as a result of mechanical shear, acid conditions or high temperature. Crosslinked starch is mostly used in food application, but crosslinked carboxymethyl starch can be used as super-absorber.¹¹

Physical modification – thermoplastic starch (TPS)

Thermomechanical deformation of starch produces thermoplastic starch or destructured starch. Destructured starch is described as a material obtained by thermoplastic melt formation, by heating starch and water, with moisture mass fraction in the range from 5 to 40 %, in a closed volume.^{12,13} The starch is heated above the melting and glass transition temperatures (t_g) of its components so that they undergo an endothermic transition. As a consequence, a melting and disordering of the molecular structure of the starch granule takes place, so that a destructured starch is obtained. The applicability of destructured starch is limited because of the degradation of starch due to water loss at elevated temperatures. Hence, the materials can only be processed by the addition of water, other plasticizers or melt flow accelerators after the granular disruption step. In order to overcome these problems, starch is mixed with an appropriated additive or plasticizing agent, such as glycerol and sorbitol, under conditions that yield a thermoplastic starch melt after thermomechanical transformations.¹⁴

In general, starch films have high tensile strength, but are brittle and exhibit almost no elongation at break. For instance, at 15 % water content, extruded starch has poor mechanical properties and is inadequate for film applications (initial tensile strength 20–30 MPa and elongation at break 10–15 %). Moreover, these properties are affected by relative humidity and thus by the corresponding changes in t_g . At low relative humidity, there are problems with brittleness, whereas at high relative humidity, with

softening. In addition to moisture sensitivity, TPS materials change their time-dependent mechanical properties (also called “postprocessing aging”). In order to overcome these limitations, different strategies are often adopted, such as:

- chemically modified starch in formulations,
- suitable plasticizers,
- association of biodegradable, renewable, or synthetic polymers to thermoplastic starch, and
- surface modifications of starch plastics.

Starch esterification by acetylation has been shown to be an efficient chemical modification for obtaining TPS-based materials with reinforced hydrophobicity and higher thermal stability. Better properties are achieved with *DS* higher than 1.7. The properties of starches modified by chemical derivatisation are also some options for TPS materials, *i.e.* they depend greatly on *DS* and the length of the introduced alkyl chain, the higher the *DS* and the longer the aliphatic chain the better are the hydrophobic properties and blends with crosslinking modified starch by hydroxyl groups and sodium trimetaphosphate.

Starch has also been widely blended with biodegradable polymers, including polycaprolactone, poly(lactic acid), polyhydroxybutyrate and poly(hydroxyester ether).^{15,16} Thermoplastic starch blended with thermoplastic polyesters, such as polycaprolactone, is the most popular base film. Commercially, TPS is used alone, mainly in soluble compostable foams, such as loose fillers and other expanded items as a replacement for polystyrene. These films are biodegradable, compostable, and fulfil the requirements of different application fields, such as packaging and agriculture.

Lignin and hemicellulose

Beside cellulose and hemicellulose, lignin is the third basic component of wood. Lignin represents a tri-dimensional branched and crosslinked copolymer of three basic phenol-propane derivatives, which are formed by biosynthesis in wood and which formulas are given in Fig. 2.

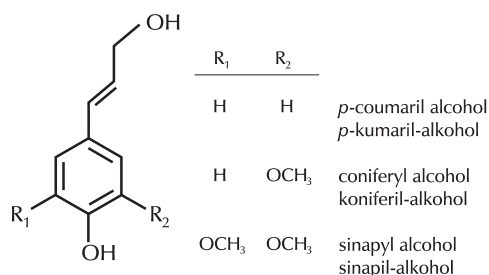


Fig. 2 – Structural formulas of three basic comonomers of lignin

Slika 2 – Strukturne formule tri osnovna komonomera lignina

Lignin is synthesised by dehydrated copolymerisation of three comonomers presented in Fig. 2. This reaction is catalysed by peroxidase bonded at the surface of cellulose fibres, and due to that, synthesised lignin is placed between cellulose fibres as well. Lignin represents a matrix in which cellulose fibres are distributed. This structure is similar to the structure of polymers reinforced with glass fibres and brings excellent mechanical properties of wood.

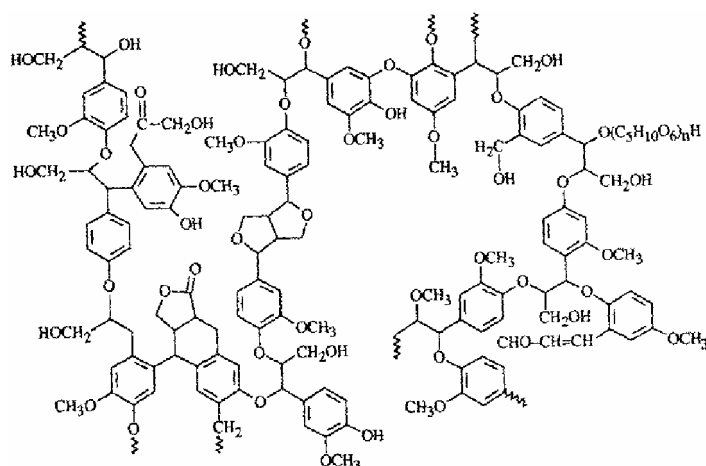


Fig. 3 – Chemical structure of lignin obtained from coniferous trees

Slika 3 – Kemijska struktura lignina iz drveta četinjače

Lignin has a quite complex structure, which mostly depends on the plant in which it is synthesised and the method used for extraction from the plant. Fig. 3 shows the model of the lignin structure obtained from coniferous trees.

The average mass fraction of lignin in wood is around 18 – 30 %. It has been estimated that plants synthesize around $20 \cdot 10^9$ tons of lignin per year. During chemical extraction of cellulose from wood, around 50 million tons of lignin per year are obtained as a side product. At the moment, the largest amount of lignin is burned directly in factories for production of cellulose fibres, in order to obtain heat energy and for the regeneration of chemicals used in the extraction of cellulose from wood. A small amount of lignin is extracted from the parent solution, and after purification it is obtained as powder and represents an amorphous, highly branched, and still partially crosslinked polymer material with t_g of about 160 °C. Lignin is hydrophobic thermoplastic polymer material, resistant to pressure but not to UV light. After adequate modification, lignin can be used: as material for production of conductive plates and other elements used in electronics and electrotechnics, heat and sound isolators, vanillin, UV – absorbers in creams for sun protection, additives used to improve cement quality, as components for production of aminoplast, phenoplast and polyurethanes, as tool for dispersion in biocide confectioning, as viscosity regulator of scum in the exploitation of oil wells, as adhesive during the briquetting of coal, etc.

The term hemicellulose represents polysaccharides of plant origin, which can be dissolved in diluted solutions of alkalis and cannot degrade under the effect of α -amylase. These are macromolecular substances, composed of a large number of monosaccharide such as hexose and uronic acids and different pentoses. The most frequent among them are xylans. The basic structure of hemicellulose is composed of β -(1,4) bonded chains of xylose. Besides that, xylans are substituted with molecules of arabinose and methyl glucuronic acid, which are non-regularly distributed along the macromolecular chains, thus contributing to the fact that hemicellulose has no crystal structure.

Up to twenty years ago, studies on the application of hemicellulose as biopolymer were insignificant. The reason being that a strong degradation of hemicellulose occurs during wood processing using sulphite or sulphate processes, leading to the formation of a large number of low molecular weight products (hexose, pentose, formic acid, acetic acid, some hydroxyl carbonic acid, resins, waxes, fatty acids, turpentine, etc.). Until now, the processes for extracting and purification of the aforementioned substances, as well as procedures for mutual fermentation of hexose and pentose were developed in order to obtain alcohol (ethanol, butanol, isopropanol and polyols such as arabitol, glycol, xylitol), organic acids (formic, acetic, butyric and lactic acid) and gases (methane and hydrogen).¹⁷

Chitin and chitosan

Chitin is a biopolymer – polysaccharide, different from cellulose only in one thing: the –OH group on C2 atom of glucose is substituted with *N*-acetylamino group. As shown in Fig. 4, chitin represents poly(β -(1 \rightarrow 4)-*N*-acetyl-2-amino-2-deoxyglucopyranose). It is formed in the shell of shellfish (crayfish and crabs and other marine animals), and insects, and can be found in the cell walls of some fungi.

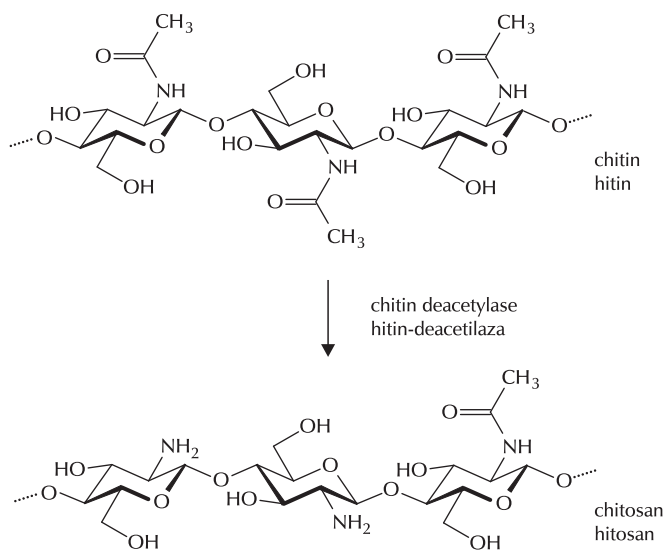


Fig. 4 – Schematic representation of macromolecular segments of chitin and enzymatic transformation of chitin into chitosan

Slika 4 – Shematski prikaz segmenata makromolekula hitina i enzimska transformacija hitina u hitozan

In the shell of shellfishes, together with calcium carbonate and some proteins, between 40 and 60 % of chitin can be built. Chitin is one of the most widespread polysaccharides in the world.¹⁸ Chitin is mostly extracted from the shell of crayfish and crabs, firstly by processing with cold HCl (5 % solution) in order to dissolve calcium carbonate, and then the obtained powder is processed with boiled NaOH solution ($w = 4$ %) in order to remove proteins. After bleaching, chitin is obtained as a white powder, insoluble in water, diluted acids, bases, and in organic solvents. The molar weight of chitin is between 1 and $2 \cdot 10^6$ g mol⁻¹. It

can be dissolved in concentrated formic acid and methane sulphonic acid. Under the influence of concentrated solution of inorganic acids, chitin degrades on acetic acid and D-glucosamine. So far, chitin has limited application in the pharmaceutical and cosmetic industries and medicine.

When chitin is processed with 40 % NaOH solution at higher temperatures or with certain enzymes at room temperature (see Fig. 4), the deacetylation of chitin occurs. After processing with alkalis chitin has 40 % or less *N*-acetylamino groups, and is called chitosan. Chitosan is the most commonly used derivative of chitin.

Chitosan is soluble in diluted solutions of inorganic acids in which it acts as polycation. The molar weight of chitosan is usually between 10^4 and 10^5 g mol⁻¹. Chitosan has a more significant application in the pharmaceutical and cosmetic industries and medicine than chitin. In addition, it is used as flocculant in water purification and as ion-exchanger, which can selectively extract heavy metals from solutions containing magnesium, calcium, potassium, and sodium.

Biopolymers obtained by biosynthesis of renewable low molecular weight and macromolecular raw materials

Glycerol, glucose, sugars, as well as products of hydrolysis of starch, cellulose and other polysaccharides are used as raw materials for the microbiological synthesis of a large number of monomers and polymers, some of which are here mentioned.

Poly(lactic acid) (PLA)

Lactic acid is a natural product that can be found in milk, sauerkraut, in human muscles, etc., but it can also be chemically synthesised from fossil raw materials. The lactic acid molecule has one asymmetric C-atom and is therefore optically active. Depending on the synthesis conditions and selected microorganisms, two optical isomers of lactic acid can be formed: L-lactic acid and D-lactic acid, as shown in Fig. 5.

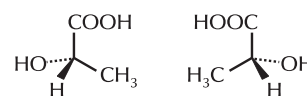


Fig. 5 – Molecular structure of L (left) and D (right) lactic acid
Slika 5 – Molekularna struktura L- (lijevo) i D-mliječne kiseline (desno)

The largest amount of lactic acid which people use today is obtained as a side product during glucose fermentation, which is usually obtained in the same process by enzymatic degradation of starch.¹⁹ Poly(lactic acid) is a polyester which is not formed in nature, but e.g. by polycondensation of lactic acid (Fig. 6a) or by polymerisation of lactide by the ring-opening process (Fig. 6b). Direct polycondensation of lactic acid is used very rarely due to the reaction difficulties as well as those in obtaining a stable product.

Poly(lactic acid) is produced in several stages in industry. In the first stage, poly(lactic acid) of low molecular weight with degree of polymerisation e.g. up to $DP = 3000$ (Fig. 6a) is obtained by polycondensation of monomer – lactic

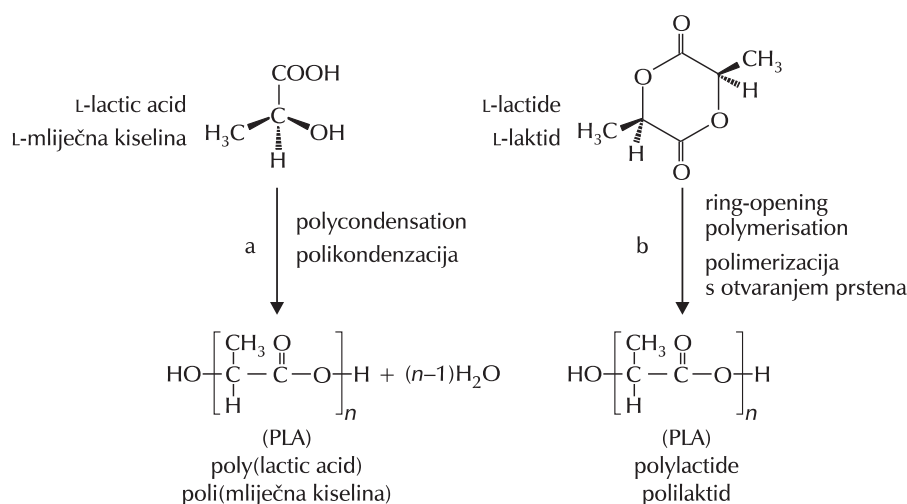


Fig. 6 – Two ways for the synthesis of poly(lactic acid), i.e. polylactide
Slika 6 – Dva puta sinteze poli(mliječne kiseline), odnosno polilaktida

acid. The water formed during this reaction – $(n - 1) \text{H}_2\text{O}$ can be removed from the reaction mixture by evaporation. The obtained poly(lactic acid) is then depolymerised at high temperature. Since the water is already removed from the reaction mixture by evaporation, the molecules of the lactic acid cannot be formed again. Instead, two monomer residues bond into ring-shaped-lactide dimer. The molecules of lactide in the presence of catalyst (powder of tin, $\text{Sn}(\text{Oct})_2$) are bonded in macromolecules of polylactide (PLA) by ring-opening process (Fig. 6b).

The starting substance for the synthesis of poly(lactic acid) is lactic acid, which appears as two optical isomers (Fig. 5). According to this, during dimer formation three forms of lactic acid dimers can be formed: L-lactide, D,L-lactide or meso lactide and D-lactide, as shown in Fig. 7.

The properties of PLA, which are important for its processing and application, depend on the structure and composition of macromolecular chains. The ratio between L and D

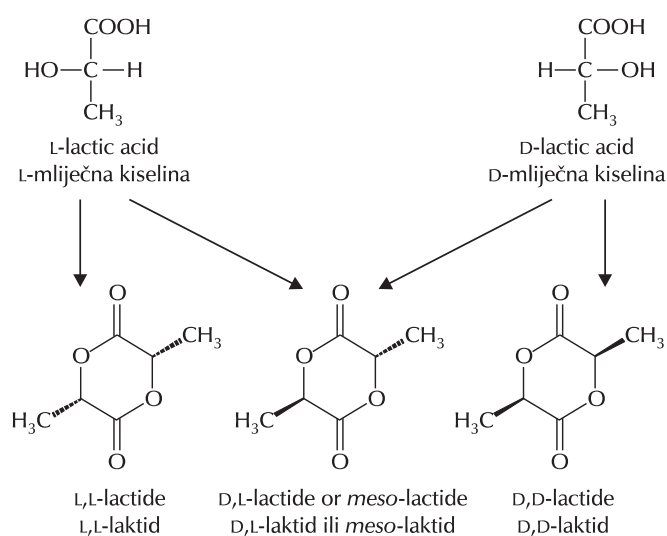


Fig. 7 – Isomers of lactic acid and resulting lactide dimers
Slika 7 – Izomeri mliječne kiseline i rezultirajući laktid dimeri

lactic acid also has special significant. For example, during polymerisation of only L-lactide, isotactic polymer is obtained. During copolymerisation of L-lactide and D,L-lactide (meso lactide), an amorphous product with a quite lower melting point than that of homopolymer and lower rate of crystallisation, is obtained. When PLLA and PDLA are mixed, the macromolecular chains of these copolymers form racemic crystals with a melting point of 190 – 240 °C. By mixing PDLA of low molecular weight with PLLA, the formed crystals act as nucleuses for PLLA crystallisation and increase its rate of crystallisation, which is very important for reducing production time e.g. using the injection technique, and for increasing shape stability at high temperature.²⁰

Depending on the applied conditions of polycondensation and polymerisation, the obtained PLA can have molar weight between 40 000 and 30 0000 g mol^{-1} . Since all properties of PLA, beside macromolecular composition, also depend on molecular weight, the selection of polymerisation conditions can have a considerable influence on its properties. Additionally, lactic acid can be copolymerised with a large number of monomers, leading to copolymers that can biodegrade very fast, but also to non-biodegradable copolymers. PLA mixes very well with some polymers, allowing preparation of blends with quite different properties, thus contributing to their increased applications, especially for production of packaging.

Thanks to the combination of properties such as biodegradability and biocompatibility, PLA is applied in medicine for production of surgical sutures and implants. It is also used in pharmacy. In recent years, large efforts have been invested in improving the properties of PLA blends, so that they can be used as technical polymers.²¹ PLA can be shaped and processed applying all the techniques that are used for the production of different subjects from synthetic thermoplastic polymers. For the sake of comparison, Table 1 lists only some selected properties of PHB, PP, PLLA and PDLA. (The first large collection of data on the properties of biodegradable polymers based on renewable vs. fossil raw materials can be found at: www.materialdata-center.com (16. 11. 2010.).

Poly(hydroxyalkanoates) (PHA)

Poly(hydroxyalkanoates) represent a group of biodegradable aliphatic polyesters, which are obtained using adequate bacteria placed on groundwork containing e.g. glucose, saharose, starch or palm oil. The procedure for the biosynthesis of poly(hydroxyalkanoates) based on glycerol, the side product formed during production of biodiesel from plants oil, has also been developed.²² The properties of poly(hydroxyalkanoates) can be varied by changing the degree of polymerisation, by changing side groups marked with R, and by copolymerisation of different monomers or by blending with other biodegradable polymers. Fig. 8 gives the general formula of polyalkanoates.

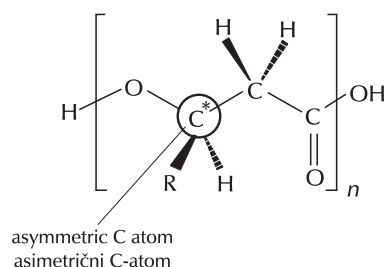


Fig. 8 – General formula of polyalkanoates

Slika 8 – Opća formula polialkanoata

From the large number of possible PHA, the widest application have homopolymers of poly(3-hydroxybutyric acid) – PHB (R = $-\text{CH}_3$) and poly(3-hydroxyvalerianic acid) – PHV (R = $-\text{C}_2\text{H}_5$), as well as copolymers of these two acids. Some plants can use bacteria *Alcaligenes eutrophus* and synthesize homopolymer of hydroxybutyric acid and its copolymer with β -hydroxyvalerianic acid and deposit as a reserve food. It is interesting to mention that the mass of this reserve food (synthesised copolymer) can be even 90 % of the dry mass of bacteria. PHB represents linear (Fig. 8), highly crystalline polyester of 3-hydroxybutyric acid ($\text{CH}_3\text{-CH(OH)-CH}_2\text{-COOH}$), with a degree of crystallisation up to 74 %. The physical properties of PHB are similar to the properties of PP (see Table 1), with only one difference – PHB is slightly stiffer and more brittle.

Table 1 – Some properties of PHB, PP, PLLA and PDLA

Tablica 1 – Neka svojstva polimera PHB, PP, PLLA i PDLA

Polymer Polimer	$t_g / ^\circ\text{C}$	$t_m / ^\circ\text{C}$	Tensile strength / MPa Vlačna čvrstoća / MPa	Bending modulus / MPa Savojni modul / MPa	Elongation at break / % Prekidno istezanje / %
PHB	4	179	40	3500	5
PP	-10	170	38	1700	400
PLLA	59	170	48	3250	2
PDLA	53	165	35	2250	5

PHB is resistant to fats, oils and water. It is permeable to gases like O_2 , CO_2 and water vapour. In the presence of certain microorganisms and water, PHB can biologically degrade completely. PHB is not only biodegradable, it is also biocompatible. Because of these two properties, PHB, just like PLA, has significant application in medicine and the pharmaceutical industry. Lately, PHB is used more often for the production of packaging, especially for food packaging. It is also used in agriculture and the paper industry. For the aforementioned applications, PHB can be shaped and processed applying all the techniques usually used to manufacture products from synthetic thermoplastic polymers.

Mechanical and thermal properties of PHB can be changed significantly by adding softeners of low molecular weight (glycerol, citric acid), and by copolymerisation with other biodegradable monomers, such as 3-hydroxyvalerianic acid. The increase in the content of 3-hydroxyvalerianic acid in the copolymer decreases melting point and degree of crys-

tallinity, and increases impact resistance. Blends of PHB with other biodegradable polymers have higher flexibility and tensile strength.

Besides PLA, PHB and PHV, special attention has been devoted to the investigation of synthesis and properties of some microbial polysaccharides such as: xanthan,²³ dextran,²⁴ and pullulan²⁵ which have practical application, and have been available on the market for a long time.²⁶

Polyurethanes are obtained by the reaction of polyaddition of multivalent alcohol (polyols) and di- or poly-isocyanate. Polyols and diisocyanates can be chemically or biochemically obtained from plant oils and saccharides or polysaccharides, and glycerol is obtained as a side product in bioethanol production. Polyurethanes synthesised using these raw materials and filled with natural fibres can be used to obtain products containing 82 % of renewable raw materials mass. The production of polyurethanes in the world is around 8 million tons per year.

Some biopolymers based on renewable raw materials which have their place in the market of polymer materials

Among the natural biopolymers, caoutchouc – cis-1,4-poly (isoprene), which is extracted from latex secreted by the plant *Hevea brasiliensis*, has a special place. Beside the large number of synthetic caoutchouc, around 40 % of mass of natural caoutchouc is used for the production of tires for transport vehicles and other articles made from rubber. Natural caoutchouc is one of the rare products based on renewable raw materials, which has for years been competitive by price and properties in relation to synthetic caoutchouc.

Colophony can be obtained in a similar manner as natural caoutchouc, only from conifer wood. This product has a very complex composition and is obtained from numerous low molecular weight substances, and as side product obtained during extraction of cellulose fibres from conifer wood. Around one-million tons of colophony is produced in the world and used directly or after the preparation of its derivatives and mixing with other polymers, mostly as industrial adhesive in different areas.²⁷

Proteins of animal origin such as casein, gelatine, collagen and albumin, and proteins of plant origin – proteins from soybean, maize and other cereal, for years have been used successfully as adhesives, especially as adhesive for labels, and some of them as thickeners for food products.²⁸

Is the use of biopolymers environmentally and economically acceptable?

About 100 million tons of polymer material based on fossil raw materials is used per year in the world for packaging production. The majority of these polymers ends up together with communal waste in landfills. To reduce the amount of landfill waste, and due to environmental and economic reasons, methods have been developed for the reuse of certain components of communal waste. For example, prior to their disposal at a landfill, polymer materials are separated from other types of waste and recycled

into “new” materials, raw materials or are burned in appropriate ovens together with other combustible types of waste to obtain energy, and only the residue remaining after combustion are disposed at landfills.

After a short or long period of use, biopolymers based on renewable raw materials and polymers based on fossil raw materials end up as waste. Biopolymers based on renewable raw materials, which are disposed of as waste can, under the right conditions, be reused by applying the three mentioned methods developed for polymers based on fossil raw materials. However, biopolymers based on renewable raw materials, which are proven to be biodegradable, can be further recycled using biological processes, such as composting (aerobic degradation) or fermentation (anaerobic degradation) and converted into useful products such as humus and/or methane.

The fact that, due to human negligence, a large amount of municipal waste, in which packaging made from polymers has a significant share, is casually thrown away on land and at sea, irritates environmental societies, which have in several countries more than once driven the initiative to prohibit the use of polymers based on fossil raw materials for packaging production, particularly for packaging of food products, in order to reduce environmental pollution (“Litter-Problems”). One such initiative was realised in Italy at the end of 2010, leading to the prohibition of using bags made from polymer materials based on fossil raw materials for carrying bought goods, particularly food products. Ecological societies and a number of uninformed politicians required that for the production of food packaging, biopolymers based on renewable raw materials that are biodegradable, compostable and in “harmony with nature”, i.e. real ecological materials should be used.

Ecological materials represent materials that require less raw material and energy for their production, application and recycling, and which pollute the environment less than other materials. Environmental and economic feasibility of applying polymer materials cannot be correctly evaluated only on the basis of data on the origin of the raw materials used for production, and its biodegradability. This question can be answered only by creating an ecological balance sheet for selected biopolymers based on renewable raw

materials, and a conventional polymer based on fossil raw materials (or any other material), which is used e.g. to produce packaging for the same product. Fig. 9 shows the order of operations used in creating an ecological balance sheet by the DIN EN ISO 14040 – 44 standard.

As shown in Fig. 9, when setting an ecological balance sheet for some materials, it is necessary first to define the goals and limits of balancing and then to develop the energy and material balance for each “phase of life” of products starting from raw materials, preparation of materials, manufacturing products which have some use value, their use, disposal to landfill or recycling. After that, it is necessary to determine the environmental impact of waste gases, wastewater, solid waste and waste produced during transport of raw materials and products. Finally, the processing of the results concerning the set of goals and their interpretation should be made. Ecological balances of the two materials, made by the same procedure, allow determining which material is ecological material and that should be done only for one purpose of the material. In addition, development of an ecological balance sheet allows proper comparison of different methods used for the production of the same product, and thus the optimal selection of the process for its manufacturing, use, and recycling.²⁹

For most applications, biopolymers based on renewable raw materials have better ecological balance than all other materials used for the same purpose. This is above all attributed to the fact that renewable raw materials (partially CO₂ neutral) are used for their production. Thus, it is not possible to make the average estimation that the application of biopolymers based on renewable raw materials is environmentally justified in all cases. For example, in a study considering the application of biodegradable polymers, made in 2008 in Austria, the results of the ecological balance sheet for application of cups for single and multiple use were presented.³⁰ Cups made from conventional polymers, such as polypropylene and poly(ethylene terephthalate), multilayer cardboard and biodegradable biopolymer – PLA were analysed. The result of this study was that multiple-use cups made from all used materials have less impact on the environment than single-use cups. The environmental pollution made by using single-use cups prepared from PLA is comparable with single-use cups prepared from PET, but compared to multilayer cardboard cups, the study suggested that PLA cups lead to higher environmental pollution. This example shows that biopolymers may not always have better ecological properties compared to synthetic non-biodegradable polymers.

When an economic balance sheet is developed in parallel with the ecological balance sheet, taking into account the costs of the raw materials and each operation in the preparation of materials and products, their use, recycling and disposal at landfills, the economic balance sheet for products made from different materials is obtained. So far, polymers based on fossil raw materials have a better economic balance sheet than biopolymers based on renewable raw materials, therefore biopolymers based on renewable raw materials are still used in areas for which the biodegradability is one of the basic properties, which ensures their application.

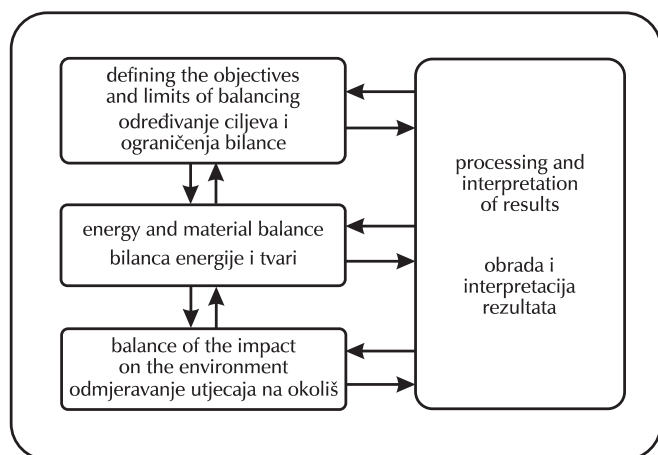


Fig. 9 – Schematic of creating an ecological balance sheet
Slika 9 – Shema izrade ekološke bilance

When it comes to biodegradable biopolymers based on renewable raw materials, it must be clearly noted that their application instead of conventional synthetic polymers cannot solve the problem of the presence of packaging and other waste in nature (“Litter-Problems”), resulting from uncontrolled disposal of used packaging in inappropriate places in the environment. Above all, the problem lies in the fact that citizens are poorly informed and thus have an unacceptable attitude toward the materials they use, as well as in the inadequate relationship between the state and waste, and the behaviour of their citizens.

In some countries, the application of bio-photo and bio-oxo degradable polymers instead of conventional polymers based on fossil raw materials for the production of bags for food products is advertised. These polymers cannot obtain the DIN EN ISO 13432 certificate, considering their ability to be composted.³¹ Using these polymers, the opposite effect than expected is achieved. When trying to compost these polymers, the environment is additionally polluted by introduction into the ground of active chemicals and fragments of molecular chains such as polyolefins, for which no data on their compatibility with nature are available and at the same time, the energy that these polymers contain is irreversibly wasted.

Researchers in the world have given great attention to the development and application of biopolymers based on renewable raw materials, but not in order to solve the problem of waste in the world (“Litter-Problems”), but primarily to reduce the consumption of deficient fossil raw materials and CO₂ emissions into the atmosphere, *i.e.* to contribute to sustainable development.

The production of food or biopolymers and bioenergy?

According to most forecasts, it is expected that around 9.5 billion people will live on the Earth in 2050. Therefore, it will be necessary to increase food production by approximately 70 % in the future, and provide suitable agricultural land. This will certainly lead to a conflict of interest between food producers, manufacturers of raw materials for the chemical industry and producers of renewable resources for energy production.

The use of agricultural land in the world will be illustrated using the example of Germany.³² In this highly developed country, 500 000 hectares of agricultural land were used in 1998 for the production of biomass for the chemical industry and energy sources, and in 2011 for this purpose 2 282 500 hectares were used. Land area of 1 966 000 hectares were used for the production of biomass as an energy source (solid fuels, bioethanol, biodiesel and biogas), and only 316 500 hectares were used to obtain raw materials for the chemical industry, of which one part is used for the production of biopolymers. The specified area is about 11 % of agricultural land. Experts in Germany have estimated that up to 20 % of agricultural land could be used for intensive production of biomass, without negative influence on satisfying the demands of German citizens for food products. The situation is similar in other developed countries, which has led to a reduction in the supply of food in the world market, and an increase in its price. In

many undeveloped countries, people are unable to produce enough food for themselves and have not sufficient money to buy more expensive food. Therefore, the World Bank has already announced the possibility of an outbreak of social unrest in 33 undeveloped countries in the world, if the food prices continue to increase in the world markets. Taking all this into account, one question arises: Is it ethical that land provided for food production for humans and animals is used for other purposes, and does that contribute to sustainable development?³³

This problem could be alleviated if people start to use land for biomass production, which is still not used to produce food for humans and animals. There are around 5.0 billion hectares of land in the world that can be used as agricultural land. For now, 1445 million hectares are cultivated and used to produce food for people (260 million hectares), food for animals (1030 hectares), for bioenergy (55 million hectares) and for production of materials (100 million hectares). The remaining 3.55 billion hectares are pastures for wild animals, and located mainly in remote areas that lacked adequate infrastructure, and in many cases lack sufficient water for intensive production of biomass. Therefore, the manufacturers of biomass as an energy source and raw material for the chemical industry prefer to use land that has already been cultivated and used for food production.

Within Interpak Fair, held in Düsseldorf from 12 to 18 May 2011, the congress entitled *Save Food* was also held, organised by the World Organization for nutrition of the United Nations (FAO). At this meeting, the results of studies on global food losses and wastage of food in the world are also presented among others works. The study was compiled by the Institute for Food and Biotechnology from Sweden on behalf of the UN.

One of the results of this study is that approximately one third of the food produced for human consumption is lost or wasted (not used for nutrition) in the world, which annually represents about 1.2 billion tons of food. This suggests that one third of the resources used for food production is lost, and that one third of the CO₂ released during the production of food pollutes the atmosphere unnecessarily. It has been noted that the foodstuffs are lost in the entire chain, starting from agricultural production to household consumption. In developed countries, the losses are the greatest in the first stage of the chain, and the smallest by end-users. The reason for the loss of food in undeveloped countries is the lack of resources and adequate techniques to harvest, pack, transport, store, and cool agricultural products, as well as the lack of proper infrastructure and marketing systems. In developed countries, food losses are the greatest at the beginning (of agricultural production) and the end of the chain, where about 30 % of prepared food are thrown despite the fact that in many cases it is still usable. According to the study, the food losses in Europe and USA per capita are between 95 and 115 kg per year. Wasted food never reaches the market and thus affects its destabilization. At the meeting, it was also possible to hear the opinion that a significant reduction in food losses in developing countries could be achieved by abolition of certain bureaucratic regulations, especially by improving the awareness of citizens as members of the consumer society.

The conflict of interest between producers of food, bio-energy sources, and raw materials for the chemical industry with a population, especially in undeveloped countries, could also be avoided or at least mitigated if developed countries begin to follow the already signed documents concerning sustainable development, especially the social components of sustainable development.

Prospects of biopolymers based on renewable raw materials

According to expert opinion, biopolymers based on renewable raw materials could replace about 70 % of synthetic polymers based on fossil raw materials in packaging production, and 10 % in other areas of application. Bearing in mind that the trend of development in the world is directed at reducing consumption of materials and energy sources based on fossil raw materials, it can be concluded that the future of polymer materials based on renewable raw materials is provided. For now, for the production of packaging from polymer materials, less than 1 % of biopolymers based on renewable raw materials are used, and their price is about two to four times higher than the price of packaging made from polymers based on fossil raw materials. In the polymer materials market, their place can find only materials with better or at least equal properties and price as already existing conventional polymer materials. How soon will biopolymers based on renewable raw materials be able to substitute polymers based on fossil raw materials depends on how fast researchers will improve their performances, increase efficiency and production capacities, and thus contribute to reducing the cost of biopolymers based on renewable raw materials.

In the last ten years, more attention has been paid to bio-renewable raw materials in the world. For example, the European Union and other developed countries are investing significant resources in so-called bio-refineries, in which new methods of separation and purification of all biomass components will be developed and used, as well as procedures for their use, primarily as a sources of raw materials for the chemical industry, food production for people and animals, and energy sources.³⁴ This will allow full use of biomass e.g. from wood, annual plants, algae, etc., which would surely result in a smaller price of biopolymers and increase their competitiveness on the market. It is interesting to mention that, also participating in the realization of these projects, beside researchers from universities and research institutes, are many experts from large chemical companies involved in the production of polymers based on fossil raw materials as their main activities (Dow Chemicals, BASF, Bayer, Breskem, Solvay, DSM, Evonik Degussa GmbH, Cereplast, etc.), which will certainly contribute to shortening the time required to transfer research results to production.

Major investment of recourses in the research and development of polymers based on biomass has already begun to yield results. For example:

– Cereplast has developed several biopolymers obtained directly from natural algae and announced their production for the end of 2011.

– Bio-oriented foils with improved properties made from PLA have been developed.

– Sulzer Chemtech has, together with collaborators, developed an innovative process and started production of PLA, which is stable at temperatures higher by about 50 °C than the standard types of PLA.³⁵

In December 2011, Ceresana published the a study of the market of biopolymers based on renewable raw materials, which describes in detail all biopolymers based on renewable raw materials, as well as the known technologies for their production. It also contains relevant data for about 87 companies that produce biopolymers based on renewable raw materials, as well as estimates of production growth in the next 10 years for all 16 biopolymers found in the market today.³⁶

Table 1 from the first part of this study,^{1,37} presents the production of biodegradable and non-biodegradable biopolymers based on renewable raw materials during 2011, and a production forecast for 2016. The following Table (Table 2) shows the world production capacities for biopolymers based on renewable raw materials in 2011, and a production forecast for 2016, sorted by region.³⁷

Table 2 – Built production capacities for biopolymers based on renewable raw materials in the world in 2011, and forecast for 2016 by region³⁷

Tablica 2 – Izgrađeni kapaciteti za proizvodnju biopolimera na bazi obnovljivih sirovina u svijetu tijekom 2011. godine i prognoza za 2016. godinu po regijama³⁷

Region Regija	Capacity in 2011 Kapacitet u 2011.	Forecast for 2016 Prognoza za 2016.
Asia	34.6 %	46.3 %
Azija		
South America Južna Amerika	32.8 %	45.1 %
Europe Europa	18.5 %	4.9 %
North America Sjeverna Amerika	13.7 %	3.5 %
Australia Australija	0.4 %	0.2 %
Total amount of biopolymers / t Ukupna količina biopolimera / t	1 167 000	5 779 000

The data presented in Table 2 are very interesting, bearing in mind that most studies and developments of biopolymers have been carried out by scientific institutions in Europe, North America and Japan, and that only around 32 % of this type of polymer was produced in Europe and North America in 2011, and it is predicted that this share will be reduced to only 8.4 % in 2016. This means that the role of Europe and North America in the production of this relatively new group of polymeric materials will be marginalised.

One carbon atom and two oxygen atoms are very tightly bounded in a molecule of carbon dioxide. A number of

papers describing the attempts to activate CO₂ and incorporate it into organic substances under acceptable conditions have been published in the literature.³⁸ Until two years ago, only Mother Nature could, from CO₂, water, some enzymes and solar energy, synthesize polysaccharides and a range of low molecular weight compounds that are all biodegradable. However, in 2010, the experts of Bayer, University of Aachen, the Center for Catalysis in Aachen, and RWE Power, producers of electric and thermal energy based on coal, synthesised a catalyst based on zinc, with which it was possible to activate and incorporate CO₂ into organic compounds, e.g. polyols, and still use them for the synthesis of polymers such as polyurethanes. At the beginning of 2011, the experts of these institutions commissioned a semi-industrial unit in the Chemical Park in Leverkusen, in which they checked the newly developed catalytic process of using CO₂ to obtain polyols, their incorporation into polyurethanes and properties of obtained polyurethanes. If the trial run is successful, it is expected that by 2015 the first factory for the synthesis of polyurethanes based on CO₂ obtained from burning fossil fuels will be started up. From a major pollutant, CO₂ will become an excellent raw material and will be included in the closed cycle of matter in nature, owing to this discovery.³⁹

List of symbols and abbreviations

Popis simbola i kratica

AGU	– α-D-glucopyranosyl unit – α-D-glukopiranozilna jedinica
CHPTMA	– (3-chloro-2-hydroxypropyl)trimethylammonium chloride – (2-hidroksi-3-klorpropil)trimetilamonijev klorid
PDLA	– poly(D-lactic acid) – poli(D-mliječna kiselina)
PET	– poly(ethylene terephthalate) – poli(etilen-tereftalat)
PHB	– poly(3-hydroxybutyric acid) – poli(3-hidroksibutanska kiselina)
PHV	– poly(3-hydroxyvalerianic acid) – poli(3-hidroksipentanska kiselina)
PLA	– poly(lactic acid) – poli(mliječna kiselina)
PLLA	– poly(L-lactic acid) – poli(L-mliječna kiselina)
PP	– polypropylene – polipropilen
TPS	– thermoplastic starch – termoplastični škrob
DP	– degree of polymerisation – stupanj polimerizacije
DS	– degree of substitution – stupanj supstituiranosti
t_g	– glass transition temperatures, °C – staklište, °C
t_m	– melting temperature, °C – talište, °C
w	– mass fraction, % – maseni udjel, %

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SAŽETAK

Polimeri na bazi obnovljivih sirovina – II. dio

S. Jovanović,^{a*} J. V. Džunuzović^b i Ž. Stojanović^c

U okviru ovoga dijela rada dan je kratak prikaz biopolimera na bazi škroba (derivati škroba, termoplastični škrob), lignina i hemiceluloze, hitina (hitozan) i na bazi proizvoda razgradnje škroba, drugih polisaharida i šećera (poli(mliječna kiselina), polihidroksialkanoati), kao i neka njihova osnovna svojstva i područje primjene. Razmatran je problem ekološke i ekonomske prihvatljivosti biopolimera na bazi obnovljivih sirovina i njihove konkurentnosti s polimerima na bazi fosilnih sirovina. Ukazano je i na probleme do kojih već dolazi zbog sve veće upotrebe poljoprivrednog zemljišta za proizvodnju sirovina za kemijsku industriju i energente, umjesto za proizvodnju hrane za ljude i životinje. Ukazano je također na optimistične procjene stručnjaka o perspektivi razvoja proizvodnje biopolimera na bazi obnovljivih sirovina.

Na kraju rada je ukazano i na uspjeh tima istraživača okupljenih oko stručnjaka tvrtke Bayer, koji su prvi u svijetu razvili katalizator, pomoću kojeg su uspjeli učinkovito aktivirati CO₂ i ugraditi ga u poliole, koje upotrebljavaju za sintezu poliuretana u poluindustrijskim razmjerima. Ovim postupkom će prvi put jedan zagađivač biti upotrijebljen kao osnovna sirovina za sintezu organskih spojeva, što će imati nesagledive posljedice na razvoj kemijske industrije, a samim tim i proizvodnje polimera.

^a Tehnološko-metalurški fakultet, Univerzitet u Beogradu, Karnegijeva 4, 11 120 Beograd, Srbija

^b Institut za hemiju, tehnologiju i metalurgiju (IHTM) – Centar za hemiju, Univerzitet u Beogradu, Studentski trg 12–16, 11 000 Beograd, Srbija

^c Henkel Srbija, AG General Industry, Henkel Adhesive Technologies, Bulevar Oslobođenja 383, 11 040 Beograd, Srbija

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