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SUSTAINABLE PLASTICS

Overpollution of environment with highly resistant to degradation petroleum-based plastics is gaining more and more attention. Development of degradable plastic materials is a promising environmentally sound solution that can reduce environmental burden, greenhouse gas emissions and dependence on petroleum resources. In this view, use of renewable biomass resources in manufacturing tailored biodegradable plastics represents a sustainable strategy for upcoming future.

Keywords: *bioplastics, petroleum based plastics, biodegradation, composites, sustainability.*

Introduction. In 1970s environmental science and environmental laws began to take their shape mainly because of growing understanding reached at that time of the damage being inflicted daily on the environment. These concerns were later formulated by United Nations World Commission on Environment and Development in 1987 as an urgent need in sustainable development which was defined as «forms of progress that meet the needs of the present without compromising the ability of future generations to meet their needs» [1]. The study also concluded that solutions to the global problems of environmental pollution and natural resource depletion require extreme changes in industrial practices [2].

Nevertheless, nowadays there is hardly a place on Earth that has not been exposed to some sort of waste. Some of these materials cause immediate hazards to humans and animals. Other wastes like plastics persist for indefinite time in the environment without degradation. In order to limit use of fossil fuels, reduce emissions of greenhouse gases and avoid pollution new biobased plastics currently are under development that are sustainable because they are grounded on renewable resources and can be decomposed under natural environmental conditions (i.e. degradable).

The aim of the article is to emphasize the necessity to replace currently used petrochemical-based plastics with new biodegradable materials obtainable from renewable resources and provide an overview of a few prospective substitutes.

Current state of plastics production. Plastics are inexpensive, lightweight and durable materials that have found wide applications in every aspect of life and industries. This resulted in tremendous rise in world plastic production from around 0,5 million tones in 1950 to 280 million tones in 2011 [3].

However, current levels of their usage and disposal can't be called sustainable and generate several environmental problems. Most conventional plastics (polyethylene, polypropylene, polystyrene, polyvinyl chloride and polyethylene terephthalate) after disposal in natural environment remain unchanged until they reach levels damaging to ecosystems.

Approximately 50 per cent of plastics are used for single-use disposable applications, such as packaging, agricultural films and disposable consumer items [4]. Now plastics comprise 12,3 % of the municipal solid waste stream, on a weight basis [5], and 20...25 % by volume [6].

At the same time there is no effective system of plastic waste management. Plastic recycling is technically difficult, involves high energy consumption and pollutants emissions; recycled products are usually inferior in quality having lower grade application and limited market. Landfilling requires large areas of land, while suitable sites become scarce worldwide. Also it becomes costly due to high environmental and sanitary requirements and still involves problems with leachate and gas emissions. Plastic waste incineration requiring high capital and operational costs is more stringent in operation and control and threaten by emission of hazardous substances (for example dioxins during polyvinyl chloride incineration) along with common carbon dioxide. Waste composting with still unfavorable economics and risk of odor and pest problem has no reliable market for end product [7].

Degradation of polymers. Degradation of polymers involves any physical or chemical change in polymer properties under influence of environmental factors, such as light, heat, moisture, chemical conditions or biological activity resulting in bond scission, formation of new functional groups and subsequent chemical transformations. Degradation has been reflected in changes of material properties such as mechanical, optical or electrical characteristics, in crazing, cracking, erosion, discoloration, phase separation or delamination. The degradation will either be photo, thermal or biological (Table 1) [8].

Table 1 – Various polymer degradation routes [8]

| Factors (requirement/activity) | Photo-degradation | Thermo-oxidative degradation | Biodegradation |
|--------------------------------|---|---------------------------------|--------------------------------|
| Active agent | UV-light or high energy radiation | Heat and moisture | Microbial agents |
| Requirement of heat | Not required | Higher than ambient temperature | Not required |
| Rate of degradation | Initiation is slow, but propagation is fast | Fast | Moderate |
| Other consideration | Environment friendly if high energy radiation is not used | Environmentally not acceptable | Environment friendly |
| Overall acceptance | Acceptable but costly | Not acceptable | Cheap and very much acceptable |

Mechanisms of biodegradation. Biodegradation of polymers results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae. Biodegradation, however, does not imply a fast process. Biodiversity and occurrence of specific polymer-degrading microorganisms vary depending on the environment, such as soil, sea, compost, activated sludge, etc. and biodegradation will not occur in unfavorable environment. It is therefore, important to couple the term biodegradable with the specification of the particular environment where the biodegradation is expected to happen, and of the time scale of the process.

Biodegradation takes place through the action of enzymes and/or chemical deterioration associated with living organisms. At least two categories of enzymes are actively involved in biological degradation of polymers: extracellular and intracellular depolymerases [8]. Chemical reactions that take place during biodegradation can be classified into two groups: those based on oxidation and those based on hydrolysis.

The first step is the fragmentation (depolymerization) of the polymers into lower molecular mass species by means of either abiotic reactions, i.e. oxidation, photodegradation or hydrolysis, or biotic reactions, i.e. degradation by microorganisms. Microorganisms excrete extracellular enzymes being able to cleave the macromolecular chains until the polymer fragments (oligomers, dimers, and monomers) become water soluble and small enough to be transported into the cells. This is followed by bioassimilation by microorganisms (use of the polymer fragments as nutrients) and their mineralization (production of inorganic substances).

Usually, the complete breakdown of large polymers to carbon dioxide requires several different organisms, with one breaking down the polymer into its constituent monomers, one able to use the monomers and excreting simpler waste compounds as byproducts and one able to use the excreted wastes. Generally, the adherence of microorganisms on the surface of plastics followed by the colonization of the exposed surface is the major mechanisms involved in the microbial degradation of plastics.

Plastics are biodegraded aerobically in wild nature, anaerobically in sediments and landfills and partly aerobically and partly anaerobically in composts and soil. Different end products are formed depending on biodegradation conditions (Fig. 1).

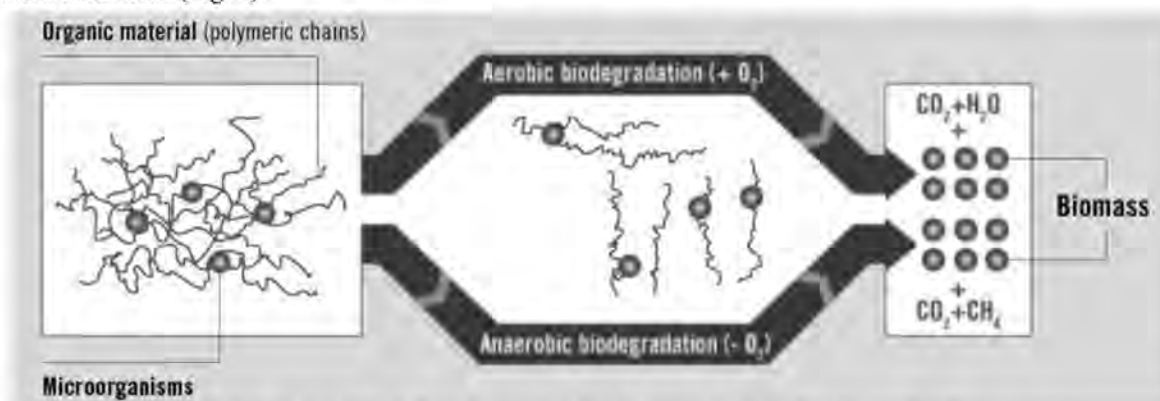


Fig. 1 – Aerobic and anaerobic biodegradation of polymers [9]

Rate of biodegradation is important and highly limited in case of compostable plastics. Compostable plastics are a subgroup of biodegradable plastics able to fragment during the composting cycle and the mineralization

process begins within the period, required for the degradation of bio-waste (e.g. grass, household waste) [10]. Fig. 2 depicts the compostability of various biobased materials. Compostability time represents the approximate period of time required for an acceptable level of disintegration of the material to occur: the original material should not be recognizable anymore in the final compost. However, composting time does not reflect the time required for the biodegradation of the materials to be fully completed.

According to European standards EN 13432 and EN 14995 a material is considered to be biodegradable if it degrades by at least 90 % within 6 months (180 days) [11].

Both the chemical and physical properties of plastics influence the mechanism of biodegradation. The surface conditions (surface area, hydrophilic, and hydrophobic properties), the first order structures (chemical structure, molecular weight and molecular weight distribution) and the high order structures (glass transition temperature, melting temperature, modulus of elasticity, crystallinity and crystal structure) of polymers play important roles in the biodegradation processes [13].

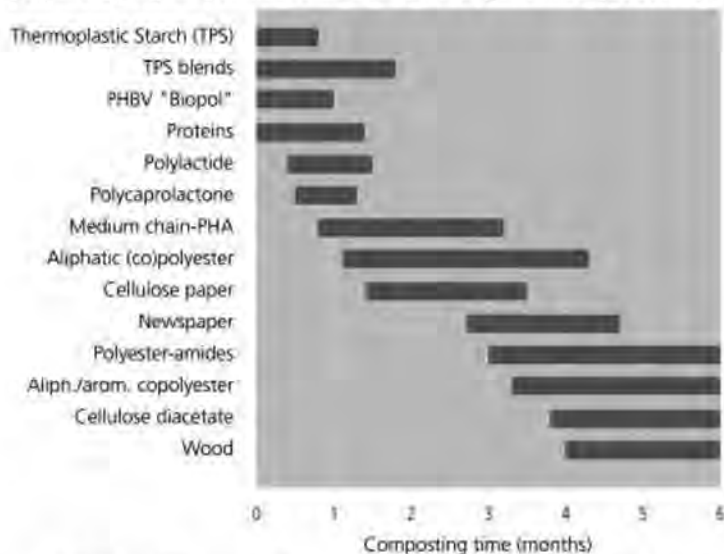


Fig. 2 – Compostability time of various biodegradable materials [12]

ral polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non renewable petroleum resources.

Different classifications of various biodegradable polymers have been proposed. The most commonly used is classification according to their synthesis process (Fig. 3) [15].

Natural polymers are formed in nature during the growth cycles of all organisms. Polysaccharides, as starch and cellulose, represent the most characteristic family of these natural polymers. Along with proteins they are the two main renewable sources of biopolymers. Another resource is lipids. To improve the mechanical properties of such polymers or to modify their degradation rate, natural polymers are often chemically modified [17]. Most conventional polymers derived from petroleum resources are resistant to degradation. Polymers with hydrolyzable backbones are susceptible to biodegradation under particular conditions. Polymers that have been developed with these properties include polyesters, polyamides, polyurethanes and polyureas, poly(amide-enamine)s, polyanhydrides [17]. Polyesters are polymers in which component monomers are bonded via ester linkages. Many kinds of esters occur in nature and the esterase enzymes that degrade them are ubiquitous in living organisms. A number of synthetic polyesters are biodegradable, such as polycaprolactone, polylactide, polylactic acid, polyglycolide, polybutylene succinate. Natural polyesters polyhydroxyalkanoates, extracted from microorganisms producing them, also used to make biodegradable plastics. Biodegradation of polymers with carbon backbones, such as vinyl polymers, requires an oxidation process for biodegradation and hydrolysis cannot occur.

Among natural polymers starch is the most extensively studied and manufactured polymer due to its complete biodegradability, low cost and renewability. Polylactic acid (PLA), a representative of biodegradable polyesters family derived from renewable resources, is the second most widely used biopolymer showing high potential particularly for packaging and medical applications. Group of synthetic polymers offers polyvinyl alcohol (PVA) as highly prospective candidate for developing sustainable plastics: it is water soluble polymer which is

However, biodegradability does not depend on raw materials from which plastic is made; therefore biodegradable polymers can be derived from both renewable resources (biomass), and from non-renewable (fossil) sources [10]. Biodegradable plastic may be referred to bioplastic which are biobased, biodegradable, or both [14]. Biobased means that the material or product is (at least partly) derived from biomass. Biomass used for bioplastics stems from plants (e.g. corn, sugarcane, or cellulose). The term biodegradable (see above) relates to a chemical process during which microorganisms convert materials into natural substances such as water, carbon dioxide and compost.

Biodegradable plastics. There are many sources of biodegradable plastics, from synthetic to natural polymers. Natu-

biodegradable, biocompatible, possessing excellent physical properties, and its production has no impact on agriculture and doesn't compete with food supply.

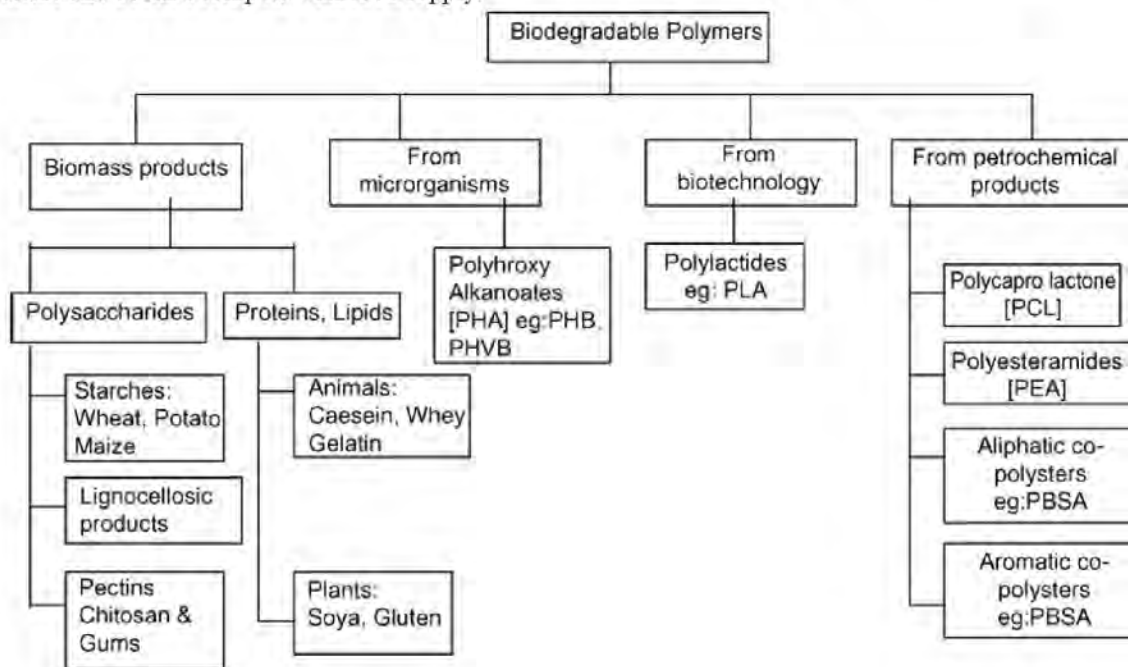


Fig. 3 – Classification of biodegradable polymers [16]

Starch is an agricultural feedstock hydrocolloid biopolymer mainly extracted from cereals (wheat, corn, rice), tubers (potatoes, manioc) and one of the cheapest biodegradable polymers. It is actually formed by two polymers: amylose, a linear and crystalline polymer, and amylopectine, a branched and amorphous polymer (Fig. 4). Starch chains show spiral shaped single or double helixes.

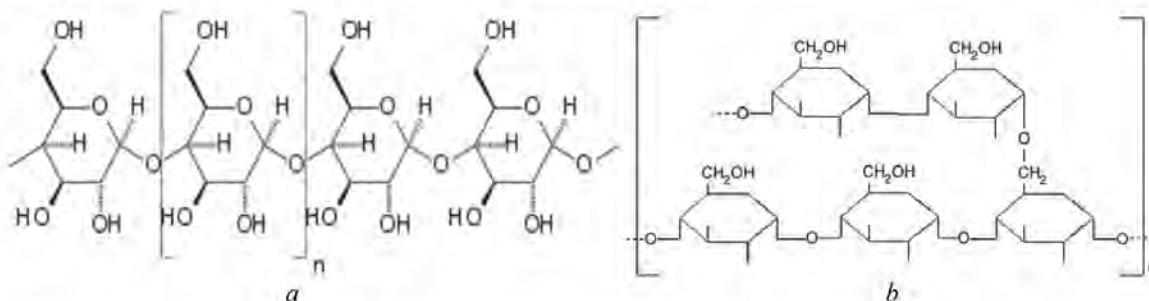


Fig. 4 – Structures of amylose (a) and amylopectine (b) [18]

Starch is totally biodegradable in a wide variety of environments. It can be hydrolyzed into glucose by microorganism or enzymes, and then metabolized into carbon dioxide and water.

Starch is usually utilized in the form of hydrophilic granules. The starch granule organization consists in alternation of crystalline and amorphous areas leading to a concentric structure. Disadvantages of using pure starch are both the brittleness and the fast retrogradation or recrystallisation. Therefore, native starch is not used directly [19]. Most starch applications require water and the disruption of the granular structure, which is called gelatinization. In order to improve its mechanical properties starch can be chemically modified. Numerous methods of modification exist, for example acetylation, oxidation, acid thinning [20]. Starch can be transformed also into a foamed material using water steam, replacing the polystyrene foams packaging material [21].

As the melting temperature (T_m) of starch is higher than its degradation temperature, it is necessary to introduce high water content or/and some non-volatile plasticizers which decrease the glass transition temperature (T_g) and the T_m , and thus thermoplastic starch (TPS), or plasticized starch can be formed. The most common

plasticizers are polyols as glycerol or sorbitol [17]. According to water content starchy materials are divided into expanded starches (between 15 and 30 % in volume) and plasticized starches, or thermoplastic starches (TPS) (below 15 % in volume) [13].

Starch-based products suffer from water sensibility, brittleness and poor mechanical properties. TPS can be blended with biodegradable polymers or fillers in order to improve the properties of plasticized starch and to conserve its final biodegradability. High amylose starch is preferred for thermoplastic film formation [22].

Plasticized starches have been combined with various fibres such as jute fibres, ramie fibres, flax fibres, tunicin whiskers, bleached leaf wood fibres, wood pulp and microfibrils from potato pulp. A high compatibility between starch and cellulose-based fibres was shown as well as water sensitivity reduction [18].

Starch has been incorporated as filler into conventional plastics, like low-density polyethylene, in an attempt to impart some level of biodegradability on the resulting composites [23]. However, such blend cannot be called biodegradable as microbial removal of starch from starch-plastic composite can only facilitate its disintegration into smaller pieces, but can't influence biodegradation of synthetic component, moreover such product is no more able to be recycled with petrochemical plastics.

TPS and polyvinyl alcohol (PVA) are highly compatible and their blends present improved tensile strength, elongation and processability compared to pure TPS. Tensile strength of the blend increases with increasing PVA concentration, and the elongation at break of the blend is almost kept constant, however their biodegradability decreases with the PVA content increase [24]. PVA with starch has shown good miscibility; both are biocompatible and consumable by microorganisms. The thermal decomposition of PVA/corn starch composites shifts slightly toward lower temperature compared to PVA, so PVA/corn starch composites suppress the thermal stability of PVA [25].

Common approaches in improving PVA/starch composites properties are chemical modification of components, surface modification and chemical or physical modifications of the PVA/starch composites during or after the blending process, such as grafting and cross-linking reactions. The cross-linking reagents and methods used in PVA/starch composites (glutaraldehyde, boric acid, epichlorohydrin, radiation, and photocrosslinking) improve the compatibility between PVA and starch molecules, resulting in the improvement of the mechanical properties, transparency and water-resistivity or swelling properties, while retaining the biodegradability [26].

Starch and polylactic acid (PLA) blends exhibit poor mechanical properties due to incompatibility, but can be improved by using compatibilizers as methylenediphenyl diisocyanate, maleic anhydride, and acrylic acid [23]. For example, mechanical properties obtained for PLA/starch blends compatibilized with maleic acid are higher than those obtained for virgin PLA/starch blends. Gelatinization of starch results in an improvement of crystallinity in PLA blends and a greater superiority of mechanical properties [17]. The mechanical properties of the starch/PLA blends are improved in the presence of PVA [24].

Blend of TPS with polycaprolactone (PCL) is similar to TPS/PLA blend in both the compatibility and the role of components. The biodegradation of PCL-starch compositions starts with the starch consumption and continuously increases with the content of the latter [27]. Blending with PCL, the impact resistance and the dimensional stability of native starch is improved significantly. The glass transition temperature and mechanical properties of TPS/PCL blend are varied with its composition and the content of plasticizer [24]. The modulus of blends of high-amylose corn starch (25 % wt.) and PCL was 50 % higher than that of PCL and the tensile strength 15% lower. At higher starch levels a very important decrease in mechanical properties is noticed [17]. Increase in starch/PCL compatibility could be achieved with the use of PCL-co-pyromellitic anhydride as compatibilizer and also by grafting PCL with maleic anhydride thereby producing modified PCL which has greater compatibility with starch. O-formylation of starch (starch modification into starch formate) could also enhance starch miscibility with PCL [23]. PCL/starch blends can be further reinforced with fiber and nano-clay respectively [24].

Typically starch aliphatic polyester blends have starch as the secondary phase. Starch is included to 30 % to aid biodegradability, lower cost and still allow for processing in extrusion or blown film lines [22].

Among reported starch based composites more successful and studied composites are those using natural fibres, nano-clay, silicates. Starch clay composites received many claims of enhanced composite mechanical properties over pure starch films [22]. Bamboo cellulose crystals were prepared and used to reinforce glycerol plasticized starch. Tensile strength and Young's modulus of the obtained composite films were enhanced and at 8 % loading level of bamboo cellulose crystals exhibited a higher reinforcing efficiency for plasticized starch plastic and considered optimal [28].

Poly(lactic acid) (PLA) is thermoplastic aliphatic polyester and is synthesized by either ring-opening polymerization or by condensation polymerization of lactic acid produced via starch fermentation from lactic bacteria (Fig. 5).

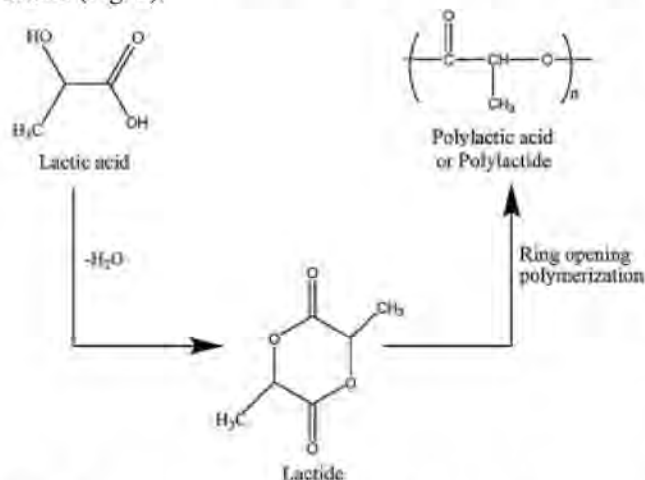


Fig. 5 – Reaction scheme to produce poly(lactic acid) [29]

bacterium *Bacillus brevis*; PLA-degrading bacteria were detected together with bacteria capable of degrading other polymers, such as PHB and PCL [30]. PLA is completely degraded under compost conditions. It is water insoluble, however microorganisms in marine environments can degrade it. Its hardness is similar to acrylic plastic [17]. Several enzymes can degrade the polymer: proteinase K, pronase and bromelain. The degradation of the polymer in animals and humans is thought to proceed via non-enzymatic hydrolysis [30].

PLA has disadvantages of brittleness and poor thermal stability. A number of low molecular weight plasticisers such as glycerol, sorbitol and triethyl citrate are used to improve its properties [31].

Many studies have been reported on PLA blends with various polymers. In most of systems, PLA and other polymers are immiscible. It is essential to compatibilize such blends to have good properties. Reactive blending of PLA with ethylene copolymer gave an important improvement of mechanical properties of PLA. This was attributed to an interfacial reaction between the components [17]. The incorporation of PLA with chitosan improved the water barrier properties and decreased the water sensitivity of chitosan film. However, the tensile strength and elastic modulus of chitosan decreased with the addition of PLA. Mechanical and thermal properties revealed that chitosan and PLA blends are incompatible [32].

The most studied natural fiber reinforcements for PLA were kenaf, flax, hemp, bamboo, jute and wood fibers. For example, the suitability of wood fibers as natural reinforcements in PLA based composites has been demonstrated in comparison with wood fiber reinforced polypropylene composites. 40 wt % content of wood fiber is able to induce an improvement of the flexural modulus, flexural strength of wood fiber/PLA composites [33]. Other studies have shown that PLA can be processed similarly to low density polyethylene and both of them work well as matrix material for natural fiber composites. Incorporation of cellulose into PLA matrix lead to stiffer but slightly more brittle and weaker materials, since Young's modulus increases and tensile strength and elongation at break slightly decrease [34].

Renewable agricultural waste lignocellulosic materials (such as bamboo husk and rice straw) were recently used as reinforcement in PLA-based composites. In particular, adding powder of water bamboo husk to PLA resulted in enhancement of mechanical properties of composite as well as in decrease of PLA glass transition temperature and last may improve the brittle characteristics of PLA [35]. Generally, the mechanical properties of PLA composites reinforced with natural fiber are improved by using surface modified fibers.

Being the second most widely used bioplastic, PLA further production development is still limited (poly(lactic acid) costs manufacturers about 20 % more than petroleum-based plastic) and also requires substantial amount of corn used as a raw material (2,5 kg of corn needed to produce 1 kg of PLA) [36].

Poly(vinyl alcohol) (PVA) is a vinyl polymer in which the main chains are joined by only carbon-carbon linkages, same as those of typical plastics (polyethylene, polypropylene and polystyrene) and water-soluble polymers (polyacrylamide and polyacrylic acid). It is the largest volume water-soluble polymer produced today

[37]. Trade names: Elvanol (DuPont, USA), Vinex (Air Products, USA), Poval and Exceval (Kuraray Co., Japan), Hi Selon (Nippon Goshei), Polyviol, Mowiol, Rhodoviol.

The main engineering applications, possibly in combination with other polymers, are films for packing chemicals, fertilizers, herbicides, disinfectants, dyes, colorants, scalers, cosmetics etc.; release films for composite moulding, solvent resistant tubes and pipes, membranes for pumps carrying petroleum or chemical products.

PVA exists only as a polymer; a monomer has not yet been isolated, so the chemical structure is shown in Fig. 6 and Fig. 7. PVA is attained via hydrolysis (or alcoholysis) of the parent homopolymer polyvinyl acetate (PVAc).

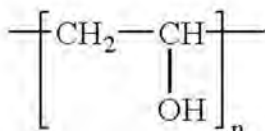


Fig. 6 – Chemical structure of fully hydrolysed polyvinyl alcohol

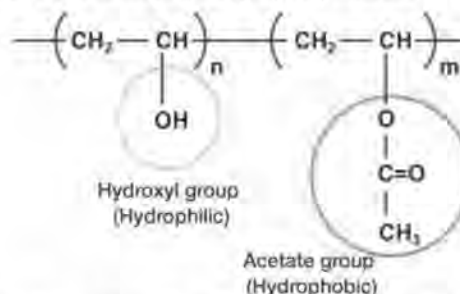


Fig. 7 – Chemical structure of polyvinyl alcohol containing residual acetyl groups

Polyvinyl alcohol is commercially available in dry granular or powdered form. Main physical characteristics are displayed in Table 2. As a hydrophilic polymer, PVA exhibits excellent water retention properties. Conditions for dissolution are governed primarily by degree of hydrolysis, and also by molecular weight, particle size distribution and particle crystallinity. Optimum solubility occurs at 87...89 % hydrolysis. The extent of hydrolysis will determine the amount of residual acetyl groups (Fig. 7) and this in turn apparently affect the viscosity characteristics [38].

Table 2 – Physical properties of polyvinyl alcohol [38]

| Properties | Values |
|-----------------------------------|--|
| Appearance | White to cream granular powder |
| Density | 1.23...1.30 g/cm ³ |
| Thermal stability | Gradual discoloration above 100° C; darkens rapidly above 150° C; rapid decomposition above 200° C |
| Coefficients of thermal expansion | (7...8) · 10 ⁻⁵ 1/°C |
| Thermal conductivity | 0.2 W/m.k |
| Yield stress | 40...50 MPa |
| Elongation at break | 100...200 % |
| Melting point | 230 °C for fully hydrolysed grades 180...190 °C for partially hydrolysed grades |
| Glass transition temperature | 75...85 °C |

The thermoplastic processing of PVA requires its plasticization with relatively large amounts of water and organic plasticizers such as glycerol, ethylene glycol and its dimer and trimer, amine alcohols, polyvalent hydroxyl compounds. PVA can be plasticized and processed by casting, dipping, injection and extrusion.

Among the vinyl polymers produced industrially, PVA is the only one known to be mineralized by microorganisms. Almost all of the PVA degrading strains belong to the genus *Pseudomonas* [30], although some do belong to other genera as *Alcaligenes*, *Bacillus* [37], *Sphingopyxis* [39]. Other bacterial strains, such as *Flavobacterium* and *Acinetobacter* were also effective in degrading PVA [40]. Mechanism of symbiotic degradation of Polyvinyl Alcohol by *Novosphingobium* sp. and *Xanthobacter flavus* was reported [41]. Several different enzyme systems involved in PVA degradation: the carbon-carbon linkage of the PVA mainchains is cleaved first by the action of either a dehydrogenase or an oxidase and this is then followed by a hydrolase or aldolase reaction [30].

Combining polyvinyl alcohol with different inexpensive degradable polymers and fillers can lead to the improvement of individual performance properties of the material, in particular cases lower its cost and enhance biodegradability. PVA is well suited to be blended with natural polymers since it is highly polar and can also be manipulated in water solution. For example, there were studied many kinds of PVA-based biodegradable composites prepared by blending PVA with starch, cellulose, chitin and chitosan, soy protein, wheat protein, egg protein, lignin and sodium alginate. Blends of polyvinyl alcohol and starch are discussed earlier.

Studies of mechanical and moisture sorption characteristics of chitosan-PVA blend films have shown that the optical properties and tensile strength of the chitosan-PVA blend films increased while elongation decreased with increase in chitosan concentration. The moisture content increased with increase in PVA concentration. The blend ratio of 80-20 was found to be the best [42].

During studying blends of PVA and wheat protein such characteristics as blends tensile strength and modulus were found to be superior to ones of gluten. However, phase heterogeneity was present in the blends and increasing PVA content could not enhance intermolecular interactions and reduced blends elongation [43].

Polymer composites using PVA as a continuous matrix and containing lignocellulosic materials from agrifood industrial waste and wood waste were investigated [44-46]. Composites of PVA (33 % by wt.) and lignocellulosic fillers, derived from sugarcane bagasse, apple and orange waste (22 % by wt.) were prepared in the presence of water and glycerol as plasticizers, and starch was added as biodegradation promoter and gluing component. Mechanical properties of composites were dependent from fibers type and plasticizers content. Composites containing apple waste and sugarcane bagasse were much harder, than ones with orange waste [45]. Studies of properties and degradation of composites made of PVA and waste wood modified by phthalic anhydride showed composites had good mechanical properties and higher durability than solid wood; also composites weight loss and mechanical properties can be enhanced by setting the phthalic anhydride/PVA molar ratio [46]. In order to reach the maximum breakdown rate of PVA based composite film lignin and starch were added as biodegradation inductors along with addition of glycerol as plasticizer. Starch and lignin can increase the biodegradation rate of PVA while preserving or improving the technical and usage properties of blends. However, the resultant compromise between composition, mechanical properties and desired optimum biodegradation was the designated blend of PVA, glycerol and protein hydrolysate containing starch [47]. Incorporation of inorganic components such as calcium carbonate and calcium phosphate could enhance mechanical properties of PVA composites [48-50].

Biodegradable polymer composites. Composites can be defined as materials that consist of two or more chemically and physically different phases separated by a distinct interface. Typically, a composite would consist of a reinforcement phase of stiff, strong material, embedded in a continuous matrix phase. This reinforcing phase is generally termed as filler. The matrix holds the fillers together, transfers applied loads to those fillers and protects them from mechanical damage and other environmental factors [51].

Most commercially produced composites use a polymer matrix material. The reinforcement materials are often fibers but can also be common ground minerals. The behavior of a composite material is explained on the basis of the combined behavior of the reinforcing element, polymer matrix, and the fiber/matrix interface. To attain superior mechanical properties the interfacial adhesion should be strong.

Biocomposites are composite materials comprising one or more phase(s) derived from a biological origin. In terms of the reinforcement, this could include plant fibers such as cotton, flax, hemp or fibers from recycled wood or waste paper, or even by-products from food crops. Further advantages are significant weight and cost savings (most cellulose fibers are cheaper and significantly lighter than commonly used glass fibers – approx. 1.5 g/cm³ compared with 2.6 g/cm³).

The manufacturing of true biocomposites demands that the matrix be made predominantly from renewable resources. The important biodegradable matrices are polyamides, polyvinyl alcohol, polyvinyl acetate, polyglycolic acid, and polylactic acid, which are synthetic as well as polysaccharides, starch, chitin, cellulose, proteins, collagens/gelatin, lignin [52].

Very thin fibres are usually used since they have a large surface/volume ratio which, in turn, has a positive effect on the adhesion between the fibres and matrix. The required quality of the fibre material depends on the desired stiffness and strength behaviour of the composite. Further selection criteria for the determination of the appropriate reinforcement fibres are maximum elongation, heat resistance, adhesion between fibres and matrix, dynamic behaviour, long-term behaviour, price and processing cost.

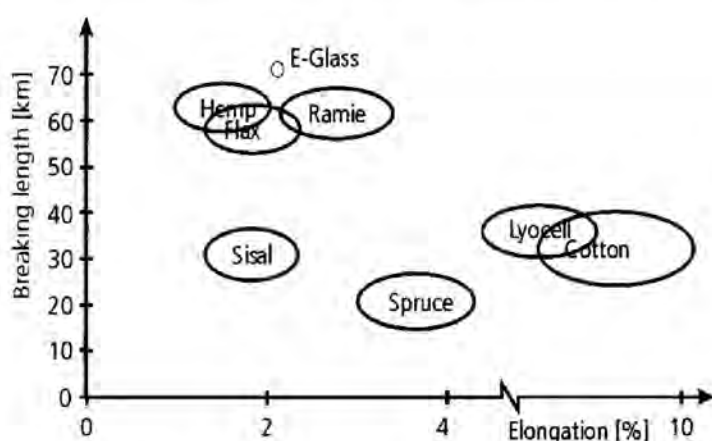


Fig. 8 – Comparison of the properties of different natural reinforcement fibers [54]

to improve the bonding at the interface. Compared to other natural fibers, banana and sisal have good mechanical properties. In general, the strength of a fiber increases with increasing cellulose content and decreasing spiral angle with respect to the fiber axis [52].

Environmental and health effects of bioplastics implementation. The main purpose of biodegradable plastics use is reducing accumulation of persistent plastic waste. At the same time switch to bioplastic materials based on renewable resources would help solving other issues associated with traditional plastics, like energy consumption, carbon emissions and adverse health effects of several plastics and additives. Conventional petroleum-based plastics manufacturing requires more energy (if fossil fuels feedstock is considered) and also followed by higher carbon dioxide emissions comparing to most biomass based plastics (Table 3).

Table 3 – Energy requirements and carbon dioxide emissions for polymer production [20]

| Type of polymer | Petropolymer | | | Biopolymer | | |
|--|--------------------------|---------------|---------------------------|----------------------|-----------------|----------------------|
| | Low density polyethylene | Polypropylene | High density polyethylene | Polyhydroxybutarates | Polylactic acid | Thermoplastic starch |
| CO ₂ emissions (kg CO ₂ /kg polymer) | 3.0 | 3.4 | 2.5 | 2.6 | 1.8 | 1.14 |
| Energy requirements (MJ/kg polymer) | 81.8 | 85.9 | 73.7 | 44.7 | 54.1 | 25.4 |

Substantial concerns have been expressed over the safety of some plasticizers, commonly used in petroleum-based plastics. Di-isonyl phthalate, a plasticizer used in polyvinyl chloride (PVC) was found to be a likely carcinogen, while vinyl chloride, the monomer of PVC, is a known carcinogen. Another plasticizer used in PVC, di (2-ethylhexyl) phthalate, was proved to be carcinogenic and it showed high toxicity in fetuses, so its use was banned in Europe. Some polycarbonates like Lexan have been found to leach bisphenol-A, a hormone disruptor that can mimic estrogen, when heated or exposed to acid. Generally hormone disruptors (chemicals that interfere with endocrine system) can cause cancerous tumors, birth defects, brain development problems, deformations of the body and later learning disabilities. Some plastics are more likely to leach monomers than others. Polystyrene has been found to leach styrene into water and food. Styrene is also a possible carcinogen and endocrine disruptor.

Bioplastics also use plasticizers like sorbitol, glycerin, and triethyl citrate. However, all three of these bioplasticizers have low toxicities. Any leaching that occurred would result in such low plasticizer concentrations that no health effects would be observed.

It's important to note that biodegradable plastics based on biomass can affect world's food supply while it becomes a limiting factor for growing population. Bioplastics derived from food crops can decrease amount of

crops that would be available for food and those derived from non food crops can compete for land with food crops. This may put pressure on food prices and increase the impact of agriculture worldwide.

Conclusions. Human society significantly benefited from the use of plastics due to their extraordinary low cost and versatility. Unfortunately, widespread use of plastics resulted in depleting fossil fuels, greenhouse gas emissions and adverse effects on the environment. Use of biodegradable plastics can be highly effective in solving these problems.

A number of materials, both natural (starch, polylactic acid) and synthetic (polyvinyl alcohol) have already shown their potential as substitutes for conventional plastics as well as their ability to completely biodegrade in environment. However, in majority of cases, they cannot be effectively used alone as single materials. On the other hand, as composite materials reinforced with various natural fibers they represent a new field for further studies and improvements of performance properties of biodegradable plastics.

However, some shortfalls of bioplastics need to be emended. For example, they cost more than petroleum-based plastics, although, the price difference can largely be attributed to the immaturity of the current technologies. Another constrain of bioplastics production is the impact on the food supply. Since bioplastics are commonly derived from food crops, shortages and price increases could result from scaled up production. Thus, bioplastics should not compete for the same land as food crops when possible. Bioplastics derived from agricultural waste or algae would have little to no impact on the food supply.

Finally, since there is a lack of necessary physical properties, further research of bioplastics manufacturing technologies is needed in order to provide a competitive sustainable product.

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Забруднення довкілля стійкими до деградації пластмасами набуває все більшого розповсюдження. Розвиток деградуючих пластмас є перспективним екологічно безпечним рішенням, що допоможе зменшити навантаження на довкілля, викиди парникових газів і залежність від нафтових ресурсів. Використання поновлюваних ресурсів біомаси у виробництві біодegradуючих пластиків є перспективним напрямом для сталого майбутнього.

Ключові слова: *біопластик, біодegradація, поновлювані ресурси, композит, сталий розвиток.*

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