

# Polymers Based on Renewable Raw Materials – Part I

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This paper gives an overview of the production and application of polymer materials based on renewable raw materials – biopolymers. It is pointed out that, investment of resources in the study of renewable raw materials in the last twenty years has led to the improvement of old and development of completely new chemical and biochemical processes for using biomass for the production of low molecular weight chemical substances, and especially for the production of biopolymers, which are biodegradable and compostable, and biopolymers which are non-biodegradable. In the same period, producers of polymers based on fossil raw materials have also developed biopolymers that are biodegradable and some of them compostable and, most important, compatible with biopolymers based on renewable raw materials. The facts considering the state of biopolymers based on renewable raw materials on the market, and prediction of production increase over the next five years are also stated. Additionally, the main renewable raw materials and the biopolymers made from them that are already present in the world market are briefly listed. A short review of biopolymers based on cellulose from wood and annual plants is also given.

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

## Introduction

In the strict sense, the term “renewable raw materials” represents crop products, *i.e.* products of biosynthesis, used in different manners to meet human needs. In a broader sense, renewable raw materials can also include products such as wool, leather, bone, fats, whey, which are formed as by-products while using basic food products of animal origin. Beside their application in the food industry, over the last twenty years renewable raw materials have gained significance as basic raw materials in the chemical industry, and consequently for the production of polymers, as well as energy sources.<sup>1</sup>

People have been using renewable raw materials practically from their existence on Earth, primarily for food, production of clothes, as building materials and for energy production. People still use renewable raw materials for the same purposes, although the purpose and the intensity of use are significantly influenced by geographical location and the development degree of countries in which they live.

The application of renewable raw materials as a starting material for production of chemical products began a long time ago. This is supported by the fact that, the recipe for soap preparation from sodium hydroxide and vegetable

oils was written on clay tablets 4000 years ago.<sup>2</sup> The chemical industry began to develop intensively 150 years ago, and in its early stages renewable and fossil raw materials were used in the chemical industry in parallel; thus around 1900 the ratio between these two raw materials was 1:1. Renewable raw materials were suppressed from the chemical industry partially by coal, and then thanks to the very rapid development of petrochemistry in the middle of the last century, renewable raw materials and coal were almost completely suppressed from the chemical industry by oil and natural gas. However, since 1980, the renewable raw materials again began to gain significance as a source of raw materials for the chemical industry. The changes in the type of raw material, used for the chemical industry, with time can be observed in Fig. 1.<sup>3</sup>

The period between 1850 and 1900 is considered as the beginning of industrial chemistry of polymer materials – “plastic”. In this period, the researchers managed to extract cellulose fibres from wood and using relatively simple chemical modification, to convert them into useful products such as celluloid, cellophane, rayon, etc. or to directly use them for paper production.<sup>4</sup> In this period, polymers were obtained also by modification of starch, polyisoprene, proteins and other natural substances, which means that in the first stage of polymer chemistry development, renewable raw materials were mostly used for polymer production.

Up to the 1950s, the synthesis of the most important standard polymers based on fossil raw materials (coal, oil, natu-

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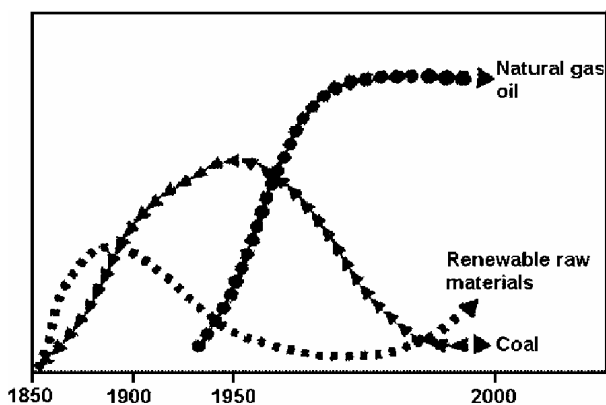


Fig. 1 – Changes in the type of raw material used in the chemical industry. Reproduced with permission from Ref. 3. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

Slika 1 – Promjena sirovinske baze kemijske industrije s vremenom. Reproducirano uz dopuštenje iz literaturnog navoda 3. Autorsko pravo Wiley-VCH Verlag GmbH & Co. KGaA.

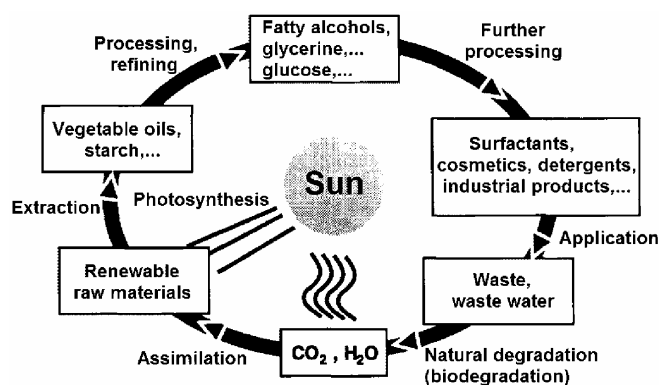
ral gas) had been developed. Parallel with the rapid development of petrochemistry in the mid-twentieth century, cost-effective monomer syntheses were also performed as well as their effective polymerisation processes, *i.e.* the intensive production of polymers based on fossil raw materials (oil and natural gas) had begun. In 1952, the first million tons of completely synthetic polymers were produced, while in 2011, 280 million tons of polymers were synthesised in the world from monomers obtained by processing crude oil and natural gas.<sup>5</sup> Such rapid production and consumption development has not been reported for any other type of material. The fast development of industrial production and consumption of polymer materials can be attributed on the one hand to the practically unlimited accessibility and relatively low price of oil and natural gas in the world market, and on the other hand, to the remarkable properties of polymer materials. Considering their price and quality, fossil raw materials as feedstock for the chemical industry and thus for polymer production, are still without competition.

Bearing in mind the fact that the world reserves of fossil resources are limited, that the world population increases daily by about 250 000, and that the energy demand of the majority of the population is constantly growing, depletion of fossil reserves is expected in the near future, even though new reservoirs of crude oil, natural gas, and coal are constantly being discovered. According to the literature, many forecasts predict the course of fossil raw materials consumption to final exhaustion. The majority predict that the production, and consequently, the consumption of fossil raw materials will peak between 2030 and 2050, and will then begin to decline, which will certainly cause an energy crisis of global proportions.<sup>6</sup> Therefore, at the end of the last century, developed countries began to invest a great amount of resources and engage a significant portion of their research capacities in the search for alternative sources of raw materials for the chemical industry. Based on the results of these studies, it was concluded that biomass, as a renewable raw material, is practically the only serious alternative to fossil raw materials. Over 170 billion tons of biomass is generated on our planet as a product of

biosynthesis, and it is quite easily accessible. From the total amount of biomass that plants synthesize per year, people are now using only 6 billion tons, or 2 to 3 %.<sup>7</sup> Materials based on biomass, *i.e.* renewable raw materials, are typically included in the closed cycles of matter in nature. Fig. 2 illustrates the formation of plant renewable raw materials, their use to obtain relevant products and their inclusion in the natural cycle of matter.<sup>3,8</sup>

Plants are capable of synthesizing renewable raw materials from water and carbon dioxide using solar energy. From the obtained raw materials, it is possible to produce an entire range of low- and macromolecular substances by different chemical reactions, which are transformed further into different final products using processing procedures. After a shorter or longer period of application, these products end up as waste, which in the presence of water and adequate microorganisms can completely degrade into the starting material: water and carbon dioxide. The fact that products based on renewable raw materials are completely included in the closed cycle of matter in nature represents their main advantage over most fully synthetic products based on fossil raw materials.

Polymers can be classified by different criteria, such as: origin, chemical composition of monomer and methods used for their bonding to macromolecules, the reaction mechanism, properties and processing methods, application areas, *etc.*<sup>9</sup> None of the current polymer classification is comprehensive and widely accepted. For example, up to twenty years ago, the concept of biopolymers included natural polymers, such as cellulose, starch and their derivatives, which are both biodegradable and compostable.



**Legend/Legenda:** processing, refining = obrada, rafiniranje; fatty alcohols, glycerine, glucose = masni alkoholi, glicerol, glukoza; further processing = daljnja obrada; surfactants, cosmetics, detergents, industrial products = tenzidi, kozmetika, deterdženti, industrijski proizvodi; application = primjena; waste, waste water = otpad, otpadna voda; natural degradation (biodegradation) = prirodna degradacija (biodegradacija); assimilation = asimilacija; renewable raw materials = obnovljive sirovine; extraction = ekstrakcija; photosynthesis = fotosinteza; vegetable oils, starch = biljna ulja, škrob

Fig. 2 – Renewable raw materials and products from renewable raw materials of plant origin as part of the closed cycle of matter in nature. Reproduced with permission from Ref. 3. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

Slika 2 – Obnovljive sirovine i proizvodi od obnovljivih sirovina biljnog podrijetla kao dio zatvorenog kružnog toka tvari u prirodi. Reproducirano uz dopuštenje iz literaturnog navoda 3. Autorsko pravo Wiley-VCH Verlag GmbH & Co. KGaA.

Synthetic polymers based on fossil raw materials were non-biodegradable. After significant investment in the development of biomass application for the production of polymers and procedures for the synthesis of polymers based on fossil raw materials, it was concluded that it would be meaningful to introduce the classification of polymers according to the origin of raw materials (renewable, fossil raw materials) and biodegradability (biodegradable, non-biodegradable polymers). According to these criteria, H. J. Endres has classified all polymers into four groups:<sup>10</sup>

- Conventional (standard) synthetic polymers based on fossil raw materials, which are non-biodegradable.
- Biopolymers obtained from renewable raw materials, which are biodegradable.
- Biopolymers obtained from renewable raw materials, but are non-biodegradable.
- Biopolymers obtained from petrochemical (fossil) raw materials, which are biodegradable.

In addition, biopolymers can have a sub-group that can be composted (aerobic degradation) or converted into biogas (anaerobic degradation), *i.e.* recycled in a certain manner. These polymers are included in the closed cycle of matter in nature according to the principal described in Fig. 2. Beside biodegradability, these polymers are important because of their composting possibility. This group of biopolymers includes: biopolymers based on starch (blends of starch), poly(lactic acid) produced by fermentation (PLA), and polyesters of PHA type (poly(hydroxyalkanoate)), *etc.* The possibility of composting for each biopolymer must be proved by appropriate standardised norms (Europe: EN 13432 or EN 14995; USA: ASTM D-6400). This group of biopolymers, as well as products made from them, must be certified by the standards specified by some relevant institution, independent of the producer, and in Germany marked with a special sign (Figs. 3 and 4), which proves that the product is biodegradable and compostable.



Fig. 3 – The designation of compostable biopolymers  
Slika 3 – Oznaka biopolimera koji se mogu kompostirati



Fig. 4 – The designation of packaging made of compostable biopolymers  
Slika 4 – Oznaka ambalaže od biopolimera koja se može kompostirati

The majority of biopolymers on the market and labelled by the sign presented in Fig. 3, is made from renewable raw materials. However, there is a group of synthetic biopolymers based on fossil raw materials, which are biodegradable and some of them are compostable, such as polycaprolactones and certain polyesters. (Biodegradability is not a function of the origin of raw materials, but the chemical composition and structure of macromolecules, *i.e.* their availability to the action of appropriate enzymes.)

Biopolymers whose macromolecules are not composed of fossil carbon, but carbon originating from renewable raw materials represent a special and completely new group of biopolymers. The basic raw materials mostly used for their production until now are: starch from maize and potato, cellulose from wood, sugar from sugar beet, and sugar cane or some vegetable oils. Biopolymers belonging to this group are mostly non-biodegradable and therefore are suitable for composting. The industrial production of different polymers based on renewable raw materials has already started: polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC) and poly(ethylene terephthalate) (PET), which are obtained from sugarcane bio-ethanol ([www.braskem.com.br](http://www.braskem.com.br)), some polyesters based on bio-propanediol, and specialty polyamides obtained from castor oil. All these polymers have the prefix *bio-*, indicating that they are synthesised from a renewable raw material, but their properties are identical to the properties of standard polymers synthesised from fossil raw materials, and therefore will not be covered in the text that follows.

### Renewable raw materials for production of biopolymers

For the production of biodegradable, non-biodegradable, and compostable biopolymers the following renewable raw materials are commonly used:

- Wood and annual plants (cellulose, lignin, hemicellulose, caoutchouc, inulin and various resins and their derivatives).
- Maize, wheat, potatoes, rice, tapioca, sunflower, rapeseed, *etc.* (starch, vegetable oils, proteins).
- Sugar from sugar beet and sugarcane (biosynthesis: PLA, PHA, dextran, pullulan, xanthan, *etc.*).
- Shell of crabs and crayfish (chitin and derivatives).
- Fat-free milk curd (casein and derivatives).
- Animal skin and bones (gelatin and derivatives).

The path from the mentioned renewable raw materials to polymers of certain practical value, can be achieved by:

- Chemical and/or physical separation of natural biopolymers from renewable raw materials (*e.g.* cellulose, starch) and preparation of their derivatives.
- Biotransformation of renewable raw materials into monomers and followed by their polymerisation (*e.g.* lactic acid → poly(lactic acid)) or by direct biotechnological transformation into biopolymers (*e.g.* poly(hydroxyalkanoate)s or xanthan).
- Chemical transformation: monomer synthesis using specific chemical reactions on native carbohydrates or oils, followed by their polymerisation or polycondensation.

### Capacity development for biopolymer production

Biopolymers are an integral part of the polymer family and are increasingly present in the global market. For example, producers of films and packaging made from polymer materials require all polymer materials with a wide range of properties in order to provide packaging for innovative products on the market and to meet the increasing demands of food and packaging manufacturers for better protection of products and prolonged stability of packed food products. The increasingly stringent environmental requirements must also be fulfilled. Table 1 shows the production volume of biodegradable and non-biodegradable polymers based on renewable raw materials, and biodegradable biopolymers based on fossil raw materials in 2011, as well as their forecasted production for the year 2016.<sup>11</sup>

Table 1 – Production of biodegradable and non-biodegradable biopolymers based on renewable raw materials

Tablica 1 – Proizvodnja biorazgradivih i bionerazgradivih biopolimera na bazi obnovljivih sirovina

Type of biopolymers Vrsta biopolimera	Production in 2011 Proizvodnja u 2011.	Production in 2016 Proizvodnja u 2016.
biodegradable biopolymers biorazgradivi polimeri	486 000 t	776 000 t
PLA	16.1 %	5.1 %
PHA	1.6 %	2.5 %
biodegradable polyesters biorazgradivi poliesteri	10.0 %	2.7 %
biodegradable blends of starch biorazgradive mješavine škroba	11.3 %	2.5 %
regenerated cellulose regenerirana celuloza	2.4 %	–
other drugo	0.5 %	0.6 %
Total Ukupno	41.9 %	13.4 %
non-biodegradable biopolymers* nerazgradivi biopolimeri*	675 000 t	5 003 000 t
bio-PE	17.2 %	4.3 %
bio-PET	38.9 %	80.1 %
bio-PA	1.6 %	1.2 %
other biopolymers drugi biopolimeri	0.4 %	1.0 %
Total Ukupno	58.1 %	86.6 %

\* Non-biodegradable polymers based on renewable raw materials also have the prefix bio-.

Nerazgradivi polimeri na bazi obnovljivih sirovina također imaju prefiks bio-.

World production of biopolymers in 2007 was 262 000 tons ([www.european-bioplastics.org](http://www.european-bioplastics.org)), and as shown in Table 1, it grew up to 1 161 000 tons in 2011, while in 2016 it is expected to reach 5 779 000 tons. The majority of biopolymers is used for packaging production.<sup>12</sup>

There are a number of factors that influence the dynamics of biopolymers production, the most important being:

- investment conditions for raising large manufacturing plants,
- development and price ratio between fossil and renewable raw materials,
- political and legal framework, which may promote or hinder the marketing of biopolymers.

H. J. Endres and co-workers collected all the relevant data on the properties of biodegradable polymers based on renewable raw materials, and compared them with the properties of conventional non-biodegradable polymers.<sup>13</sup> Based on these findings, they concluded that the properties of these two groups of polymers are comparable and that biopolymers based on renewable raw materials can already, in e.g. the production of packaging materials, replace 70 % of conventional polymers. (For the packaging production, around 100 million tons of conventional polymers are used today.) The price of biodegradable polymers based on renewable raw materials is 2 to 4 times higher than the price of non-biodegradable polymers based on fossil raw materials, which are used for the same purpose. However, the price of biopolymers based on renewable raw materials will certainly drop after technological improvement and their increased production. Thus, expectations are that these biopolymers will soon also compete in price with polymers based on fossil raw materials.

### Areas of biodegradable biopolymer applications

Biopolymers are used in areas where they have the best functionality and in which they have bypassed properties in relation to environmental protection. In most developed countries it has been shown that, consumers are very positive about the application of biopolymers, and not only for packaging production. The following products made from biopolymers based on renewable raw materials have a strong production increase trend:

- Biopolymer sacks and bags used for the collection of bio-waste, and which can be composted together with bio-waste, thus allowing other application. By using packaging made from biopolymers to collect bio-waste, the total quantity of bio-waste increases. This relieves the landfills, improves the composting process and the quality of the obtained compost.
- Biologically degradable foils which can be used, for example, to cover the land on which different fruits and vegetables are planted. After use, these foils can be left on the agricultural land and ploughed.
- Packaging for food for serving at major events, or used for selling on the streets or serving in a plane. This packaging can be composted after use along with the food remains.
- Foils for short-term food packaging, which allow good presentation and viability of product. Simple composting is

a recommendation for the good sales of these materials. In this manner, decaying food from supermarkets can be composted without separation from the biopolymer packaging. Bottles, cups and other containers made from biopolymers such as PLA are used for drinks without carbon dioxide or for dairy products.

- Biopolymers are permeable to oxygen, resulting in extension of storage time of some food products packed in biopolymer containers, which increases consumption of biopolymers for the production of such packaging.
- There is significant application of biopolymers in medicine (surgical sutures, implants) and in the pharmaceutical industry.
- Composite materials based on biopolymers and cellulose fibres (for example) are used more often in the production of transport vehicles and construction.

### Biopolymers based on cellulose

Cellulose is a natural macromolecular substance – biopolymer, which can be found e.g. in cotton fibres (96 %), hemp (67 %), jute (64 %), etc., or as composite with lignin and hemicellulose in wood (35 – 50 %). Plants synthesize cellulose by photosynthesis starting from  $\text{CO}_2$  and water. Therefore, cellulose belongs to the group of polysaccharides, which are biodegradable. These polymers are the most frequent substances in the total biomass, synthesised by plants. The following text points out the molecular and supramolecular structure, which together allows the direct use of cellulose as natural biopolymer, and cellulose derivatives to obtain biodegradable and compostable biopolymers for different purposes. More information about cellulose and its use can be found in a review paper from *Klem and co-workers*, and the literature cited there.<sup>14</sup>

Cellulose macromolecules are linear and composed of glucose molecules (monosaccharide), that are bonded by  $\beta$ -1,4-glucoside bonds as shown in Fig. 5.

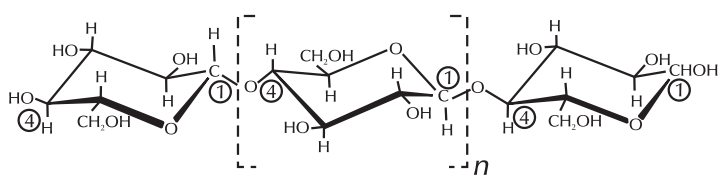


Fig. 5 – Structural formula of cellulose macromolecule

Slika 5 – Strukturna formula makromolekula celuloze

The size of cellulose macromolecules is characterised by the molecular weight or degree of polymerisation –  $DP$ , i.e. the average number of glucose molecules bonded by covalent  $\beta$ -1,4-glucoside bonds in a single macromolecule ( $DP = n + 2$ ; Fig. 5). The  $DP$  values of cellulose depend on its origin and how its separation and purification was performed. For example, cellulose extracted from algae *Valonia* has a degree of polymerisation of about 40 000, from unopened cotton capsules 14 000, from various species of wood about 1700, and decomposed for preparation of derivatives around 200.<sup>15,16</sup>

The majority of cellulose properties depends not only on its chemical structure of macromolecules, but also on its sup-

ramolecular structure. Namely, due to the presence of three free hydroxyl groups on each basic structural element of cellulose – glucose, hydrogen bonds appear inside one macromolecule (intramolecular bonds) and between different macromolecules (intermolecular bonds) as shown in Fig. 6.

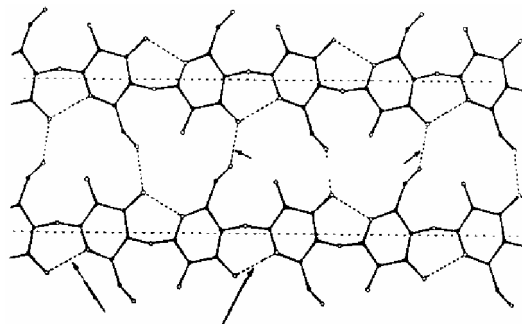


Fig. 6 – Parts of two macromolecular chains of cellulose and the possible inter- (indicated by short arrows) and intramolecular hydrogen bonds (indicated by long arrows)

Slika 6 – Dijelovi dvaju makromolekulskih lanaca celuloze i moguće inter- (označene kraćim strelicama) i intramolekulske vodikove veze (označene duljim strelicama)

The hydrogen bonds formed inside one macromolecule (intramolecular bonds) contribute to the reduction of flexibility, i.e. increase the stiffness of the macromolecular chains. The intermolecular hydrogen bonding also leads to the parallelisation of macromolecular chains of cellulose, and formation of fibril (elemental fibrils, microfibrils, bundles of microfibrils) crystal structure. The degree of crystallisation depends on the origin and the method applied for cellulose extraction, which for chemically extracted cellulose fibres from wood is around 45 %, and up to 80 % for cellulose from algae *Valonia*.<sup>17</sup> The melting temperature ( $t_m$ ) of cellulose is higher than its degradation temperature. Therefore, pure cellulose cannot be used as a thermoplastic polymer. However, cellulose in the form of cotton fibres, as well as fibres from hemp, flax, etc., have already been directly used for hundreds of years for the production of textile, which is further used for clothing, sails, packaging (sacks, bags) for different products. In addition, cellulose fibres with a lower or higher content of lignin or hemicellulose, extracted from wood or annual plants using different methods, have also been directly used for over 2000 years for paper production. In 2010, around 393.9 million tons of paper, cardboard and cans were produced in the world.<sup>18</sup>

It is interesting to point out that paper, the production of which started more than 2000 years ago, when the molecular structure of cellulose and the existence of macromolecular substances were unknown, is still being researched as part of a separate science of cellulose fibres and paper production technology, and is practically not classified as a biopolymer material.

The swelling ability of cellulose in water is very low; it is practically insoluble in standard solvents and cannot be melted, so the application of cellulose as a thermoplastic polymer is not possible. In order to use cellulose as a thermoplastic polymer, it has to undergo chemical modifica-

tion. Therefore, cellulose is chemically modified in order to obtain cellulose derivatives soluble in most solvents, and soluble at higher temperatures. This is achieved by transformation of cellulose into esters or ethers using adequate reactants.<sup>19</sup>

### Esters and ethers of cellulose

Of the organic cellulose esters, the most important are cellulose acetate (CA), cellulose propionate (CP), and cellulose acetate butyrate (CAB). The formulas of the most commonly used organic cellulose esters are given in Fig. 7.

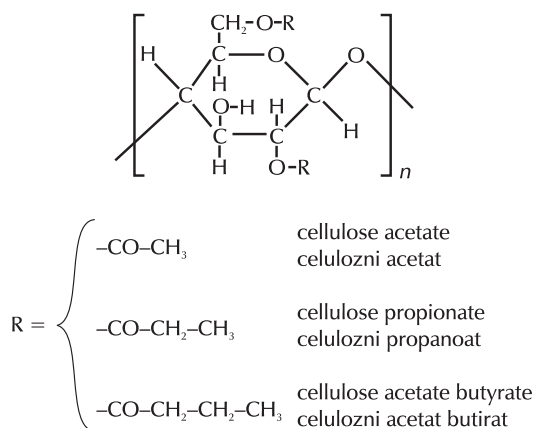


Fig. 7 – Formulas of selected cellulose esters

Slika 7 – Formule izabranih estera celuloze

These cellulose esters are produced from pure bleached cellulose fibres, extracted from wood or from the remaining cotton fibres on cotton seeds, by reacting with a mixture of acetic acid anhydride and acetic acid, or acetic acid chloride, for example. Cellulose triacetate was well known in 1865, but due to its very poor solubility and high melting temperature, it found no practical use. In 1904, it was found that cellulose acetate, which has a substitution degree between 2.0 and 2.5, is soluble in available solvents (acetone, ethyl acetate, methyl acetate), can be melted easily, and can be used as a thermoplastic polymer. Cellulose acetate can be processed easily into foils with good mechanical and optical properties or into fibres. Cellulose acetate is now mostly used for the production of fibres and foils, usually in combination with low molecular-weight softeners or in combination with one or two cellulose esters – CP or CAB. In addition, CA is used variously in the cosmetic and pharmaceutical industries. Cellulose acetate fibres are utilised for the production of textile, cigarette filters, foils, membranes, and different types of filters, and isolation lacquers.

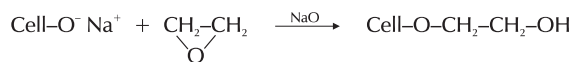
Cellulose ether has been an industrial product for seventy years already. The following ethers have found the most application: methylcellulose (MC), carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), and some mixtures of cellulose ethers. Etherification is performed in two stages. In the first stage, which is common for all etherification reactions, the cellulose is activated with NaOH or KOH, leading to the formation of alkali cellulose. In the second stage of the reaction, adequate reactants are added

to the formed alkali cellulose, such as methyl chloride, ethylene oxide or chloroacetic acid leading to:

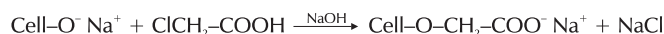
methylcellulose



hydroxyethyl cellulose



or carboxymethyl cellulose



Cellulose ethers have found their application in the textile, food and pharmaceutical industries, in the production of paper, detergents, paints and synthetic polymers, adhesives, and in the exploitation of oil.

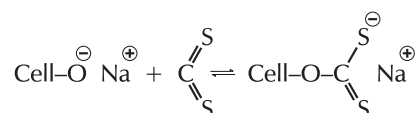
Cellulose ethers and esters with a high substitution degree usually act as thermoplastic polymers, but in that case their biodegradability is reduced. It has been shown that by grafting biodegradable polymers on cellulose or on some of its derivatives, it is possible to improve both thermoplastic behaviour and biodegradability.<sup>20</sup> Numerous cellulose derivatives is described in literature, but their application possibilities are limited.<sup>21</sup>

### Regenerated cellulose

#### Viscose process

According to the produced amount, the most important cellulose products besides paper are those produced from regenerated cellulose: chemical cellulose fibres and foils (cellophane). Since cellulose is insoluble, its processing into a certain type of product is performed from a solution, after production of cellulose derivatives.

The process of producing cellulose xantogenate, soluble in alkalis, was developed around 100 years ago.<sup>22</sup> Cellulose xantogenate is produced by processing pure cellulose, chemically extracted from wood, with the solution of  $w(\text{NaOH}) = 10 - 25 \%$ , leading to the formation of alkali cellulose. After removing the excess NaOH solution, alkali cellulose is exposed to oxygen, which leads to the degradation of cellulose macromolecules, and reduction of polymerisation degree to 300 – 400.<sup>23</sup> Thus prepared alkali cellulose, is added carbon disulphide ( $\text{CS}_2$ ) forming cellulose xantogenate:



The obtained cellulose xantogenate is then dissolved in water solution of  $w(\text{NaOH}) = 6 \%$ . In order to obtain foils, the solution containing  $w = 7.0 - 8.5 \%$  cellulose xantogenate, must be squeezed through an adequately shaped nozzle into a bath of sulphuric acid, e.g., containing the following salts:  $\text{Na}_2\text{SO}_4$  and  $\text{ZnSO}_4$ . When squeezing it into the bath, coagulation of cellulose xantogenate and formation of foils first occur, followed by secession of xantogenate groups, and release of  $-\text{OH}$  groups, i.e. regeneration of cellulose. The foil obtained from such regenerated cellu-

lose – cellophane, then must be washed, dried and confectioned. The same process, using a different nozzle, is applied for the production of fibres from regenerated cellulose. Around 1980, about 2.2 million tons of fibres were produced in the world from regenerated cellulose – viscose.

The processes for the production of cellulose ethers and esters, as well as regenerated cellulose (viscose) were developed at the turn of the 20<sup>th</sup> century. Since then, these processes have improved technically, but still lead to significant environmental pollution, especially the process used for producing regenerated cellulose. Due to complicated and expensive production, and several ecological reasons, cellophane is being replaced more and more by packaging materials made of synthetic polymers or other biopolymers.

### Lyocell process

The processes used for the production of cellulose derivatives and regenerated cellulose are highly developed in the world; however, none of these processes could find application in the industry.<sup>24</sup> Twenty years ago, the situation changed when a completely new process for the production of regenerated cellulose was developed without previous preparation of cellulose derivatives. In this process, cellulose is directly dissolved in a mixture of solvent *N*-methylmorpholine *N*-oxide (NMMO)/water, and foils and fibers are formed from the solution. This process, called the Lyocell-process, found its application in the industry very rapidly.<sup>25</sup> The Lyocell-process is the most simplest way to produce regenerated cellulose, in which the solvent is regenerated during the work and used again, practically without losses, so the whole process is performed producing minimal air and water pollution. In Fig. 8, the formula of NMMO molecule is presented.



Fig. 8 – Formula of *N*-methylmorpholine *N*-oxide (NMMO)

Slika 8 – Formula *N*-metilmorfolin-*N*-oksida (NMMO)

Due to the presence of strong N-O dipole in combination with water, NMMO can directly dissolve cellulose without previous activation or formation of derivatives. The real solvent for cellulose is NMMO-monohydrate (13.3 % of water). The dissolution is performed by dispersing cellulose into the mixture of NMMO and water (e.g. 50 % of water), and then at higher temperature the water evaporates until the content of 13.3 % is reached, i.e. until NMMO-monohydrate is formed, which dissolves cellulose very fast. The application of the Lyocell-process was made much easier after the discovery of efficient stabilizers, such as propyl-3,4,5-hydroxybenzoate, which prevents degradation of NMMO and cellulose at higher temperatures, usually used for the production of foils and fibres (80 – 120 °C). As in the case of the viscose process, the cellulose solution (8 – 20 %) is squeezed through an adequately shaped nozzle into a water bath in which the cellulose almost instantly participates. Then, NMMO is separated from this

bath and after purification can be reused almost without losses (recovery of 99.6 %). Fibres and foils made from cellulose using this process have much better properties than those produced using the viscose process, and therefore the application possibilities of regenerated cellulose are slowly increasing. It is expected that this revolutionary process will contribute to the significant increase in the application of products made from regenerated cellulose.<sup>26</sup>

### List of symbols and abbreviations

#### Popis simbola i kratica

CA	– cellulose acetate – celulozni acetat
CAB	– cellulose acetate butyrate – celulozni acetat butirat
CMC	– carboxymethyl cellulose – karboksimetil-celuloza
CP	– cellulose propionate – celulozni propionat
Cell	– cellulose – celuloza
HEC	– hydroxyethyl cellulose – hidroksietil-celuloza
MC	– methylcellulose – metil-celuloza
NMMO	– <i>N</i> -methylmorpholine <i>N</i> -oxide – <i>N</i> -metilmorfolin- <i>N</i> -oksid
PE	– polyethylene – polietilen
PET	– poly(ethylene terephthalate) – poli(etilen-tereftalat)
PHA	– poly(hydroxyalkanoate) – poli(hidroksialkanoat)
PLA	– poly(lactic acid) – poli(mliječna kiselina)
PP	– polypropylene – polipropilen
PVC	– poly(vinyl chloride) – poli(vinil-klorid)
DP	– degree of polymerisation – stupanj polimerizacije
$t_m$	– melting temperature, °C – talište, °C
w	– mass fraction, % – maseni udjel, %

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## SAŽETAK

### Polimeri na bazi obnovljivih sirovina – I. dio

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U okviru ovoga rada dan je pregled stanja u proizvodnji i primjeni polimernih materijala na bazi obnovljivih sirovina – biopolimera. Ukazano je na to da su ulaganjem sredstava u izučavanje obnovljivih sirovina u posljednjih dvadesetak godina unaprijeđeni stari i razvijeni potpuno novi kemijski i biokemijski postupci uporabe biomase za dobivanje niskomolekulskih kemijskih supstancija, a posebno biopolimera koji su i biorazgradivi i kompostabilni, ali i biopolimera koji su bionerazgradivi. U istom razdoblju su i proizvođači polimera na bazi fosilnih sirovina razvili biopolimere koji su biorazgradivi, a neki i kompostabilni i što je vrlo bitno kompatibilni s biopolimerima na bazi obnovljivih sirovina. Navedeni su i podaci o stanju na tržištu biopolimera na bazi obnovljivih sirovina, kao i procjene povećanja proizvodnje u sljedećih desetak godina. Pored toga ukratko su prikazane osnovne obnovljive sirovine, kao i biopolimeri koji se od njih proizvode i već su prisutni na svjetskom tržištu. Dan je kratak prikaz biopolimera na bazi celuloze iz drveta i jednogodišnjih biljaka.

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