ISSN 1070-3632, Russian Journal of General Chemistry, 2017, Vol. 87, No. 6, pp. 1357–1363. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © V.V. Myasoedova, 2015, published in Rossiiskii Khimicheskii Zhurnal, 2015, Vol. 59, No. 3, pp. 36–43.

Agro-Polymers and Biopolyesters

V. V. Myasoedova*

Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kuusinena 15, Moscow, 125353 Russia
**e-mail: veravm777@gmail.com*

Received December 1, 2015

Abstract—The interest in bio-based and biodegradable products has increased recently, following the depletion of fossil fuels and aggravation of environmental problems all over the world. Replacement of nondegradable synthetic polymers by biodegradable polymers brings about a 10–20% per year expansion to the market of environmentally pure and friendly composites and materials. A lot of researchers take part in studies on biodegradable polymers. According to their synthesis route, structure, properties, and application areas, biodegradable polymers are classified into agro-polymers (including cellulose, starch, chitin, and protein) and biodegradable polyesters: poly(lactic acid), poly(hydroxyalkanoates). So-called biopolyesters were synthesized from fossil fuel resources, but the modern trend is towards obtaining the main products from renewable resources.

Keywords: agro-polymers, biopolyesters, biodegradability, renewable resources, clean technology and ecology

DOI: 10.1134/S1070363217060378

In recent decades, there has been an increased interest in biodegradable polymers following the advancement of the concept of sustainable development and growth of importance attached to environmental issues. As a result, the market potential of this environmentally friendly product line is rapidly growing at 10–20% per annum. This is interconnected with enhancement of the technological priority potential of both agro-polymers and biopolyesters, with the result being that biodegradable polymers have become an important exploration trend not only in science but also in marketing.

Due to extensive use in industry and agriculture, synthetic polymers are essential for modern. Most synthetic polymers that were developed on the basis of fossil fuel resources are incompatible with the environment, since they cannot be incorporated into the natural recycling system. Much effort has been undertaken to examine the properties, especially thermophysical, of environmentally friendly (“green”) polymers and to expand their practical applications. The latter include those in the form of biofuels, which are in the focus of one part of this review (mainly based on author’s patents and articles), with the other part dedicated to studies on biodegradable polymers and composites thereof. The development of green polymers chemistry and technology is relevant both scientifically and practically, being a key to sustainable development that can support our comfortable life. Russia is known to be rich not only in fossil fuel resources but also in bioenergy resources, with 9% of the world’s total reserves of annual lignocellulosic materials resting on its cultural arable lands and 25% of the world’s timber reserves (perennial lingocellulosic materials), on its forests. Fossil fuels dominate in the fuel balances of transport and heat and power generation sectors. The Energy Strategy of Russia until 2020 (approved by the RF Government Decree no. 1234 of August 28, 2003) highlights the need for more active use of different types of waste (including wood and chemical production/agriculture residues) in heat and power production and sets a goal of increasing the share of renewable energy sources in the total energy consumption to 7% after 2020. Russia’s technical potential of biomass energy amounts to 53 mln tons of coal equivalent. Table gives examples of environmentally friendly polymers.

Circulation of polysaccharides, saccharides, and lignin in nature is shown schematically in Fig. 1 and the table.

Lignocellulosic raw material-based renewable energy sources can provide a wide range of energy

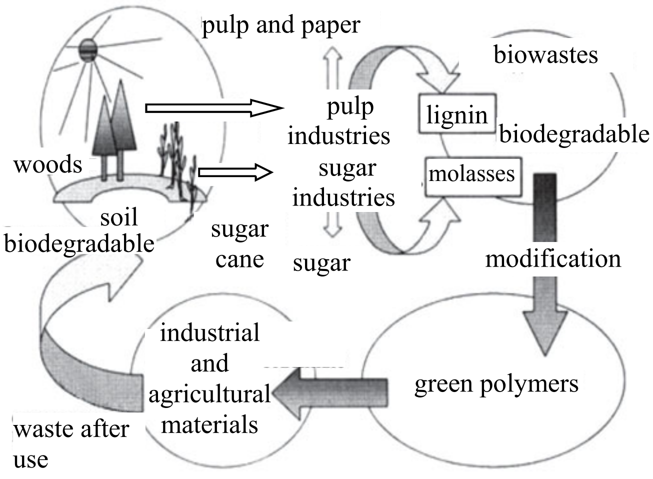


Fig. 1. Circulation of lignin- and saccharide-based synthetic polymers in nature.

services over a long period of time: reliable supplies of heat, power, and energy for transport without producing greenhouse gas emissions and climate effects (as required under the Kyoto Protocol). According to some estimates, a partial transition from fossil fuels to biomass in Russia would save from 10 to 20 mln tons of fossil fuel resources and coal per annum; moreover, carbon dioxide emission reduction will be achieved. The use of biomass would stimulate additional investments for regions and as a result would create new jobs. Currently, biomass-based energy production in Russia follows two main lines: use of wood chemical industry and wood processing waste for heat and power generation, production of fuel pellets (mostly for export) and briquettes for domestic market; production of liquid biofuels for transport: biodiesel and bioethanol.

Large stocks of plant raw materials whose waste is a potential source of fuel are held by Russian enterprises; previously they were not a marketable product for both the domestic and European markets due to a number of difficulties associated with low bulk density (80–250 kg/m^3) and high humidity specific to biomass waste. These are difficulties in regards to storage, transportation, combustion (completeness), etc.; they can be overcome via increasing the bulk density and heat effect of combustion by granulation, i.e., via production of fuel pellets. Despite the development of the fuel pellet production sector and relevant optimistic forecasts, a number of obstacles still prevent widespread distribution of biomass-based energy production (both in Russia and in the EU countries). Renewable raw materials for solid biofuels are cellulose-lignin mixtures composed of nonperennial agricultural and perennial plants: wood (waste wood, pieces, chips, sawdust, powder) and pulp and paper industry waste, as well as animal wastes in pelletized or briquetted form, which are a kind of raw material for industrial production. Not only solid fuel for furnaces, fireplaces, and boilers of autonomous dwellings, small and medium-sized thermal power plants are produced from biomass but also liquid or gaseous fuel for transport.

The European Commission’s Renewable Energy Directive sets a goal of tripling the renewable energy production over the next 10 years. The share of biofuel would increase to 74% of the total contribution from renewable energy sources. In recent years, the production of granulated biofuel in Western Europe, North America, and Japan has increased dramatically. By contrast to the initial biomass, biogranules are characterized by relatively high bulk density (600–700 kg/m^3), low humidity (<10%), and relatively high heat of combustion.

The author and her team have developed and patented formulations and technologies for the production of fuel pellets, granules, and briquettes both on the basis of renewable raw materials. The latter included

Examples of “green” polymers

Polymer types	Examples
From microorganisms	Polysaccharides such as xanthan gum, alginic acid, hyaluronic acid, and gellan gum Polyesters, e.g., poly(hydroxyalkanoates)
From plants	Polysaccharides, e.g., cellulose, starch, carrageenan, locust bean gum. Cellulose esters, e.g., cellulose acetates Saccharide-based polyurethanes and polycaprolactone derivatives. Starch
Form animals	Collagen, chitin Chitin and chitosan-based polymeric derivatives and composites

sawdust and other wastes from the wood chemical and wood-processing industries, and waste from pulp and paper mills and agro-industrial complex, as well as any carbon-containing compounds from coal, peat, and oil refining waste [1]. Pilot-industrial testing of new formulations and production processes for fuel pellets is under way now. Together with our partners that have available the equipment for production of pellets and briquettes, we are planning to continue these efforts. A number of monographs on natural biopolymers which are biomass components were published in Russia and abroad [2, 3]. Advantages and novelty offered by fuel pellets in comparison with traditional fuel products consist in the following:

(1) Suitability of renewable raw materials (biofuels), which are a type of industrial fuel, as both a basic material and a binder. Solid plasticizer, a binder, by contrast to liquid binding agents like adhesives, as well as to hot water and steam, ensures improvement of all performance characteristics of briquettes/pellets:

– Higher strength (and reduced crumbling);

– Improved surface gloss and, in some compositions, increased whiteness;

– Higher density of ≥ 1.2 g/cm^3;

– Longer burn duration (smooth burning, giving off no fumes);

– Increased calorific value (heat of combustion);

– Lower energy costs, due to lower pressure during pressing and to “dehumidification” relative to the moisture content of the raw material;

(2) Environmental friendliness, with only negligible amounts of CO_2 (and a small amount of ash residue from combustion, like in natural decomposition of wood) being emitted and with briquette/pellet burning being involved in the natural cycle of substances;

(3) Significantly increased calorific value compared to briquettes/pellets based on secondary carbonaceous raw materials (1.5 times that of wood-derived fuel products); by up to 80–90% higher efficiency of briquetted/pelletized fuel compared to coal and wood; possible conversion of the energy produced, e.g., of heat energy to power; approximately 3.5 times lower costs of heat supply of residential and industrial premises with briquettes/pellets compared to power supply;

(4) Multifunctionality and suitability for combustion in residential and industrial boilers, in power installations of heating and power stations, or, e.g., for use as a sorbent;

(5) Being demanded by the European market: exportable products;

(6) Relatively high bulk density (600–700 kg/m^3), low humidity (<10%), and a relatively high heat of combustion of biogranules (an average of 16–18 MJ/kg, up to 30 MJ/kg in accordance with RF patent no. 2015106105, 2015), by contrast to the initial biomass; and

(7) Autonomy: due to low fire hazard, both storage and transportation are convenient (owing to high bulk density of the briquettes/granules); feeding-loading into boiler and generation of heat energy can be automated.

The EU Biomass Action Plan of the Commission of the European Communities points out that the EU currently meets 4% of its energy needs from biomass, which share would increase to 20% by 2020. The energy balance of the Russian Federation will be dominated by fossil fuels as before.

Figure 2 shows the scheme for classifying biopolymers into agro-polymers (polysaccharides, proteins) and biopolyesters, that can be obtained by extraction from microorganisms or from biotechnology (by synthesis from bio-derived monomers) and also can be prepared from petrochemical products (synthetic monomers). At present, three groups of the most promising natural polymers are used for developing biodegradable structural and functional materials: poly-α-hydroxy acids (polylactide and its copolymers), polyhydroxyalkanoates (poly-3-hydroxybutyrate, PHB, and its derivatives), and polysaccharides (cellulose, chitin, chitosan, etc.).

The structures of the most widespread biopolymers depicted by chemical formulas are shown in Fig. 3.

The structure of the exopolysaccharide kefiran synthesized was published by us in [4].

The advantages offered by poly-3-hydroxybutyrate (PHB), chitosan (ChS), and the like over traditional synthetic materials are independence from oil and gas resources, renewability in nature, and biodegradability meaning ecological and biological safety. We uphold the view that classification of biodegradable polymers is to be based on the polymer synthesis route. Poly-3-hydroxybutyrate is an extensively used model for crystalline state physics and for applied research and

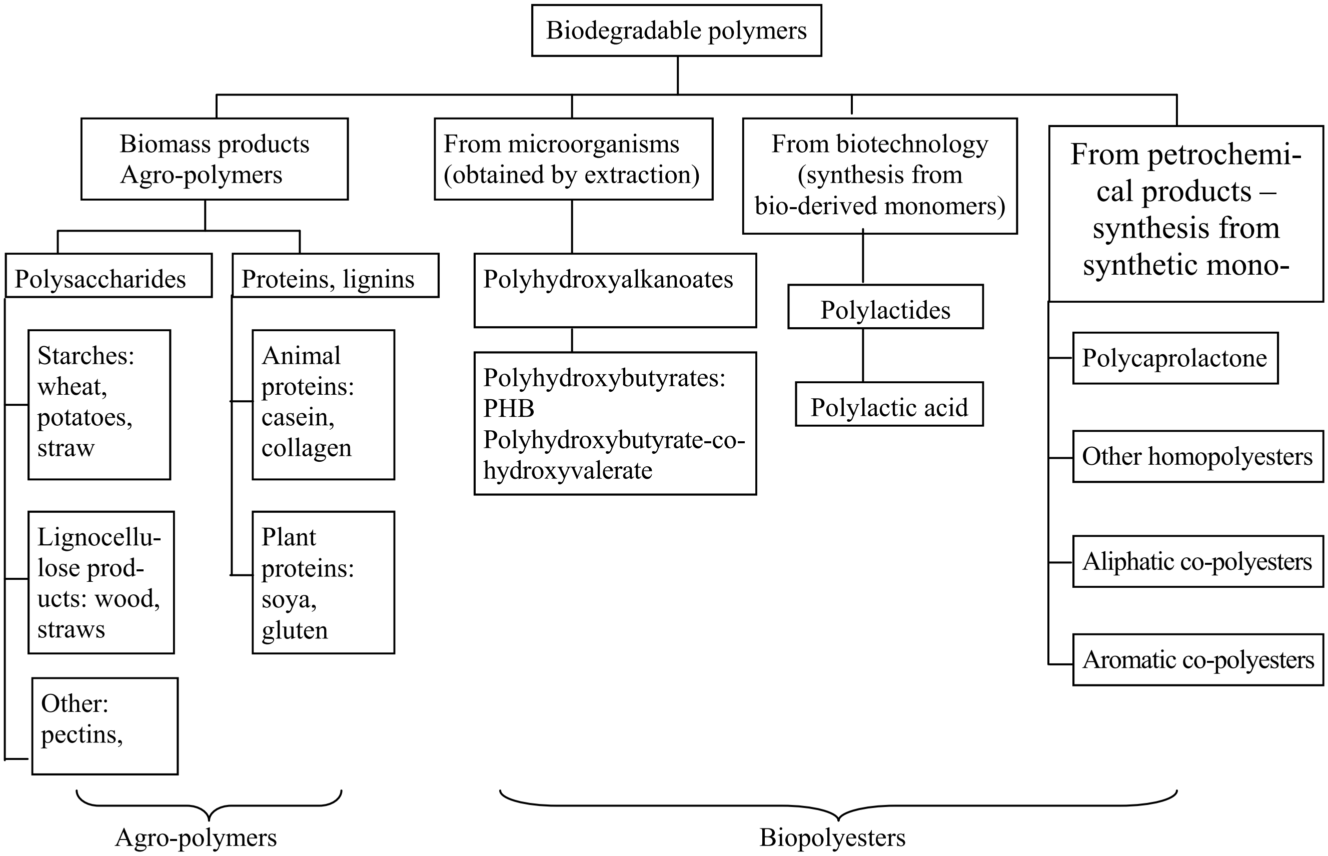
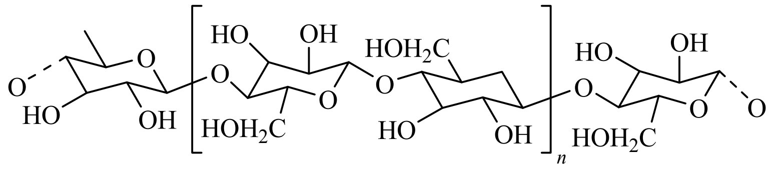
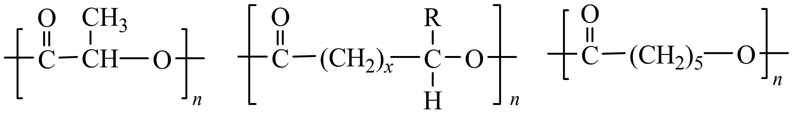


Fig. 2. Agro-polymers and biopolyesters.

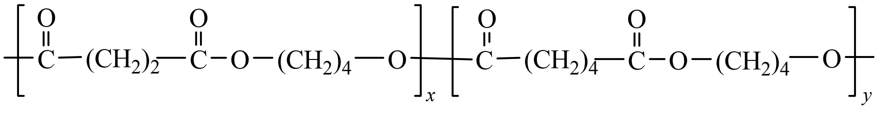
development in designing selective barrier materials for biodegradable packaging, as well as in cell engineering and designing a new generation of therapeutic systems for targeted drug delivery. The mechanical characteristics of PHB can be improved through modification either by biotechnological processes, via copolymerization with 3-hydroxyvalerate, 3-hydroxyoctanoate, and the like monomers, or by preparation of mixed compositions with other materials. The procedure for PHB mixing with ChS offers advantages of complete biodegradability of the resulting compositions into environmentally safe nontoxic products (H_2O, CO_2), biocompatibility, and promise for application as matrices for targeted and prolonged delivery of encapsulated drugs in medicine. The above-mentioned “green” polymers, e.g., poly(ε-caprolactone) (PCL) and polyurethane derivatives, were synthesized from lignin, saccharides, and cellulose. Thermal properties of these polymers can be characterized by various physicochemical methods, including thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA). Also, combinations of these methods with other, in particular, spectral methods, e.g., Fourier transform IR-spectrometry (FTIR), as well as TG-DTA, are used. With cellulose and lignin being the main components of plant raw materials, the molecular structure of both these biopolymers has received particular attention for the last 100 years [2, 3]. The crystalline structure of cellulose was studied by X-ray diffraction analysis and by solid-state nuclear magnetic resonance (NMR) spectrometry. On the other hand, higher-order structures of lignin in the amorphous state have scarcely been studied, since analytical methods were limited. Recently, the supermolecular structure of biopolymers has been studied at the nano level, as atomic force microscopy (AFM) provided a possibility to observe individual molecules and molecular assemblies. This technique directly visualizes the heterogeneity of the both biopolymers in the crystalline or amorphous state. Moreover, the morphological observation data can be analyzed jointly with the results of other physical



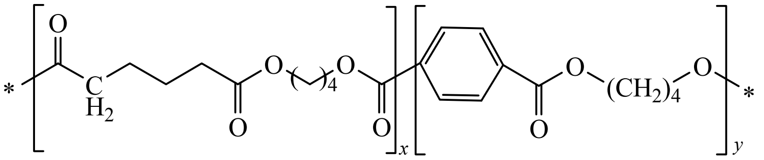
Cellulose



Polylactic acid Polyhydroxyalkanoate Polyhydroxyalkanoate



Poly(butyleneccinate-co-adipate)



Poly(butylene adipate-co-terephthalate)

Fig. 3. Chemical structure of the biopolymers.

measurements. AFM was used to observe the supermolecular structure of cellulose and lignin through using their water-soluble derivatives, carboxymethylcellulose (NaCMC) and sodium lignosulfonate (NaLS). The latter served as samples whose aqueous solutions were spread on a freshly cleaved mica surface and examined by AFM. The AFM images of NaCMC clearly reveal rigid strands; the thickness of the strands occurring in mono- or double layers is ~0.7 nm, and the width of the strands ranges from 15.2 to 18.2 nm. With X-ray diffraction patterns taken into account, these data reveal that 4–5 molecules were bundled.

Common raw materials for synthetic "green" polymers are molasses and lignin. Molasses produced from sugar cane and beet is a brown viscous liquid. The chemical components of molasses are sucrose and saccharides: glucose and fructose. Molasses typically finds industrial application an ingredient in fermentation and also is used as livestock feed. However, it was found to be suitable as a raw material for the synthesis of polyurethane- and polycaprolactone-based saccharides. Molasses is derived from cane sugar in tropical and subtropical regions; on the other hand, beet molasses is produced in cold regions, e.g., in Russia. About 130 mln tons of sugar is currently produced in the world per annum. The production of molasses makes up to 30% of that of sugar. Therefore, the world molasses production can be estimated at >40 mln tons per annum, which is more than sufficient for the production of environmentally compatible biopolymers at the present time and in the future. As to lignins, they are derived from renewable resources: trees, plants, and crops. Almost 30% of wood is constituted by lignin. Lignins are nontoxic and versatile in their physicochemical and performance characteristics. Most industrial lignins are obtained in the pulping process of cellulose from sulfite pulp. Kraft lignin is typically burnt as fuel in pulping mills. Abundant lignin quantities are formed from the process of hydrolysis in alcohol production. Nearly 30 mln tons of lignin is produced globally per annum. However, this is only an estimate produced in the absence of reliable statistical data, because lignin is often burnt immediately after production. About one million tons of water-soluble lignosulfonate derivatives, which are byproducts of sulfite pulping, find use in Japan as chemicals, e.g., as dispersants. Commercial lignin is a byproduct of the pulping industry, as mentioned above, and is mainly isolated from wood in a chemical pulping process. Typically, lignins are natural random network polymers whose physical and chemical properties vary depending on the extraction processes. The higher-order structure of lignin, which consists of phenylpropane units, is amorphous. Three phenylpropane monomers, coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol, combine to form a three-dimensional network in the process of radical-based lignin biosynthesis. For the above reason lignin does not have such a regular structure as cellulose; this is a physically and chemically heterogeneous material whose chemical structure is not known exactly. With each lignin molecule bearing more than two hydroxy groups, lignin-based polyurethane derivatives, polycaprolactone derivatives, and epoxy resins can be obtained using functional OH groups. Cellulose is a polysaccharide made up of $C_6H_{10}O_5$ units [2]. For the specific features of thermochemical conversion of cellulose and its derivatives, see our previous study [5].

Degradability and degradation of agro-polymers and polyesters occurring in the environment can be caused by various factors and processes: oxidation, hydrolysis, mechanical and thermal degradation, photodestruction, biodegradation. Biodegradability is determined on the basis of several field and laboratory tests including, in accordance with the appropriate ASTM, measurements of the physicomechanical parameters and the chemical composition of the degradation products resulting from aerobic and anaerobic degradation of a polymer in various media [7]. This concerns, e.g., PHB, which is a storage polymer formed in the cells of certain microorganisms under unbalanced nutritional conditions. Due to biodegradability, which is one of its most attractive commercial properties, PHB is extensively used as a model object in different applications, as already been mentioned above. So-called polyesters can be synthesized from fossil resources, but many types of biopolyesters are produced from renewable raw materials. Of particular interest are their modification techniques. For example, the mechanical characteristics of PHB were improved by modification in two different ways [9]: at the biotechnological level, by copolymerization with 3-hydroxyvalerate and 3-hydroxyoctanoate monomers and by creation of compositions with synthetic polyester epsilon-PCL and other, or via preparation of mixed compositions with other materials. A number of studies were dedicated to PHB degradation in natural ecosystems such as soil, compost, and water bodies [10], as well as of PHB composites with other materials. As already mentioned, an advantage of the procedure of PHB mixing with ChS [10, 11] consists in that it yields compositions that are completely biodegradable to nontoxic environmentally safe products (H_2O, CO_2) and also biocompatible and promising for medicinal applications as matrices for targeted and prolonged delivery of encapsulated drugs. In the furtherance of the fundamental goal of creating a new generation of completely biodegradable composite systems as a replacement of traditional synthetic materials, amphiphilic, completely biodegradable compositions based on natural polymers, hydrophobic PHB and hydrophilic chitosan, have been developed. By contrast to the known polymeric therapeutic systems, the systems proposed offer an increased sorption capacity for drugs, as well as controllable rate of biodegradation in model media and suitability for different kinetic profiles of prolonged release of drugs over a broad range of timespan (from weeks to months) [13]. Also, successful efforts were undertaken to develop compositions from components substantially differing in polarity. These systems are promising for encapsulation and targeted delivery of biologically active compounds over extended period of time. Moreover, they combine in a unique way the biocompatibility and biodegradability without formation of toxic products. Such systems only need to be tested for adhesion to metal surfaces of cardio-implants (coronary stents, pacemaker electrodes) to be suitable as potential coating materials for local drug delivery. Chitosan is the only cationic polysaccharide that has a primary amino group in practically every unit, which determines its biological activity and also makes it the most attractive among the polysaccharides series for chemical modification applications [6]. Due to film- and fiber-forming ability and unique sorption and complexing properties, ChS and its derivatives hold promise for development of ion-exchange membranes to be used in ultrafiltration dialysis as special sorbents and flocculants, implants, and drug carriers in the form of gels, nano- and microparticles, blended fibers, sponges, and other matrix forms. For biotechnologies employing immobilized enzymes and pH-sensitive therapeutic agents, improved solubility of the polymer matrix under physiologically acceptable conditions is desirable. The most effective way to making ChS soluble in both aqueous and organic media without compromising its biochemical properties is grafting synthetic polymers with different hydrophilicities to the main chain of the polysaccharide [13].

Much attention is being currently paid to the effect of the nature of polymers on compatibility with polyesters, as well as to the physicochemical properties of the resulting mixtures. For example, some formulations of polyester-cellulose nitrate mixtures have been studied. Using the glass transition temperature as the criterion of the compatibility of polymers it was found that polyesters: poly(epsilon-polylactone), polylactide, poly(valerolactone), poly(ethylene adipate), and poly (butylene adipate) are compatible with cellulose nitrates containing 12.62 and 13.42% nitrogen, and poly(α-methyl-α-propyl-β-propyolactone) and poly(α-methyl-α-ethyl-β-propyolactone),incompatible with cellulose nitrates. The first group of polyesters owe their compatibility with cellulose nitrates to hydrogen bonding between the carbonyl groups of the polylactide and the carbonyl groups of cellulose nitrates, which is stronger than self-association in individual cellulose nitrate. Moreover, there exists evidence for intensive dipole-dipole interaction between the carbonyl groups of the polyesters and the nitro groups of cellulose nitrates.

The author and her team have obtained new materials based on low-density polyethylene and polypropylene with agro-polymer additives (cellulose, soya flour, spent grains), which possess the required set of performance properties and are biodegradable under environmental conditions. The new approach to estimating biodegradation by the DSC method can be used for more in-depth analysis of the processes occurring both in polymers and in composite materials during bioconversion. The effect of soil on polymer-filler compositions was also evaluated by Fourier-transform IR spectroscopy using the absorption bands at 3360 and 1730 cm^{-1} [14].

The world market of biopolymers is developing extremely rapidly. Biopolymers that have received the most widespread use in the world now are starch-based polymer, whose share is 40% of the consumption. About one-third of the total consumption is accounted for by cellulose and polylactic acid (15% each) and 10%, by polyesters.

REFERENCES

1. Myasoedova, V.V., RF Patent 2015106105, 2015; Myasoedova, V. et al., EU Patent 1 090095, 2003.
2. *Physical Chemistry of Non-Aqueous Solutions of Cellulose and Its Derivatives*, Chichester: Wiley, 2000.
3. Myasoedova, V.V., *Fizicheskaya khimiya nevodnykh rastvorov tsellyulozy i ee proizvodnykh* (Physical Chemistry of Non-Aqueous Solutions of Cellulose and Its Derivatives), Moscow: Nauka, 1991.
4. Gradova, N.B., Khokhlacheva, A.A., Murzina, E.D., and Myasoedova, V.V., *Biotekhnologiya*, 2014, no. 6, p. 18.
5. Myasoedova, V.V., Shchegolikhin, A.N., and Rozhkova, O.V., *Entsikloped. Khim.-Tekhnol.*, 2010, no. 4, p. 18.
6. *Khitin i khitozan. Poluchenie, svoistva i primenenie* (Chitin and Chitosan: Production, Properties, and Application), Skryabin, K.G., Vikhoreva, G.A., and Varlamov, V.P., Eds., Moscow: Nauka, 2002.
7. Steinbuchel, A., *Biopolymers,* Weinheim: Wiley, 2003, vol.10: *General Aspects and Special Applications*.
8. Swift, G., *Biodegradability of Polymers in Environment, FEMS Microbiol. Rev*., 1992, vol. 103, p. 339.
9. Ivantsova, E.L. and Iordanskii, A.L., *Pharm. Chem. J.*., 2011, vol. 45, no. 1, p. 51. doi 10.1007/s11094-011-0559-1
10. Bonartseva, G.A., Myshkina, V.L., Nikolaeva, D.A., Rebrov, A.V., Gerasin, V.A., and Makhina, T.K., *Microbiol.,* 2002, vol. 71, no. 2, p. 221. doi 10.1023/A:1015162608031
11. *Environmental Silicate Nano-Biocomposites, Green Energy and Technology*, Avérous, L. and Pollet, E., Eds., London: Springer, 2012. doi 10.1007/978-1-4471-4108-2_2.
12. Lesnyakova, L.V., Vikhoreva, G.A., Gal'braikh, L.S., Akopova, T.A., and Zelenetskii, A.N.., *Fiber Chem.,* 2012, no. 3, p. 149. doi 10.1007/s10692-012-9418-4
13. Ivantsova, E.L., Kosenko, R.Yu., Iordanskii, A.L., Rogovina, S.Z., Prut, E.V., Filatova, A.G., Gumargalieva, K.Z., Novikova, S.P., and Berlin, A.A., *Polymer Sci.m Ser. A,* 2012, vol. 54, no. 2, p. 87. doi 10.1134/S0965545X12020058
14. Lukanina, Yu.K., Kolesnikova, N.N., Myasoedova, V.V., Popov, A.A., and Khvatov, A.V., *Kompozity polietilen/poroshkovaya al'fa-tsellyuloza* (Polyethylene/Powdered alpha-Cellulose Composites), Chetvertaya vserossiiskaya Karginskaya konferentsiya *"Nauka o polimerakh 21-mu veku"* (Fourth All-Russian Kargin Conf. "The Science of Polymers to the 21st Century"), 2007, Moscow, p. 162.