Development of a Biodegradable Additive from Brown Algae of the Russian Far East for the Production of Plastic Packaging

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Abstract
The article presents the development of a biodegradable additive from brown algae of the Russian Far East for the packaging polymer industry. We consider a possibility of using cellulose derived from algae of the Primorsky Krai, as an additive to polymeric packaging products, which impartsthe properties of biodegradability to the polymer. A way to produce the biodegradable additive for plastic packaging is to reduce the duration of the technological process, increase the yield and quality of the end product and expand the resource base through the use of cheap and non-traditional local raw materials.
Keywords Biodecomposition; Biodegradation, Brown algae; Biodegradable packaging, Polymeric materials.

1 Introduction

Russia annually produces about 70 million tonnes of municipal solid waste (M-SW), the major share of which (more than 50%) refers to packages. Up to 10 thousand hectares of land is annually alienated for MSW landfills and dumps. This land also includes fertile lands, withdrawn from the agricultural use. Currently, in the Russian Federation measures to implement new investment projects in the sphere of solid waste management are developed and being taken[1]. Only 3% of this amount are recycled, and the rest are incinerated or disposed of in landfills. However, incineration is an expensive process that also leads to the formation of the highly toxic (such as furans and dioxins) compounds.

Time needed for degradation of packaging materials in natural conditions may range from a few decades to hundreds of years, the use of biodegradable materials in the packaging industry will lead to a significant reduction of this period. Therefore, the topic of the development of biodegradable materials is relevant and is of practical and scientific interest.

Polymeric materials have become part of our lives and have replaced wood, metal, glass, ceramics. A large number of scientific papers and reviews[2-20] are dedicated to the studies on the degradation of polymers. According to the International Organization for Standardization, biodegradable plastics are polymers the degradation of which takes place under the influence of microorganisms, bacteria and fungi. The use of such plastics minimizes the adverse effects on the environment ecology. The degradation rate depends on a number of factors such as the type of a polymer, the type and concentration of degrading materials, moisture, temperature and a series of other factors. The corresponding public opinion and the legislative ways of control and regulation contribute to the accelerated proliferation of the production technologies of these packaging materials. In many countries, the government prohibits the use of plastic bags and disposable plastic utensils made of traditional types of plastic, and one has to pay for plastic bags in supermarkets, while paper bags are free.

In recent years, the production of packaging materials is the leading sector of the economy and is growing worldwide, including in Russia. Based on this, one of the relevant directions is the production of environmentally friendly biodegradable packaging. The development of new highly efficient technologies, the creation of products based on plant raw materials, their further assimilation and standardization become more popular due to the wide spectrum of biological effects. Particular attention is paid to the need to use local plant raw materials with sufficiently large natural reserves of natural or cultivated natural sources that are promising in terms of their introduction into production.

One of the ways to produce biodegradable materials is to create composite materials based on natural biodegradable polymers such as cellulose, chitosan, gelatin, polypeptides, casein, and others.

This research work aims to study the possibility of using local plant raw material - brown algae of the Primorsky Krai in order to create a new biodegradable polymeric composition, which along with the high molecular basis comprises organic fillers (starch, cellulose) that should serve as a nutrient medium for microorganisms. The advantage of biogenic packaging made using local algae lies precisely in the high speed of growth - some species can grow up to a meter during twelve hours.

2 Main part

At the Department of Commodity Research and Examination of Goods of the Far Eastern Federal University, the work was undertaken to develop a method for producing cellulose from brown algae of the Primorsky Krai. The main objective of the development was to provide an efficient method for producing cellulose from sea algae, mostly of the Fucus genus, the use of which as a raw material makes it possible to clean coastal areas littered with the cast ashore algae and improve their ecological condition.

Today, modern biotechnology is aimed at the production of both traditional and new types of substances and materials. In addition, at this point, renewable plant raw materials can become a solution. Such technology can be successfully used for the further development of the industry in the Far East.

Today, many physical and technical characteristics of biodegradable polymers are not inferior to the characteristics of conventional plastics. Biodegradable polymers are degradable in natural conditions under the influence of such environmental factors as light, temperature, humidity and with the participation of living microorganisms as well. Simultaneously, high-molecular substances degrade into low molecular ones, which are safe for the environment. Another positive characteristic of biopolymers is that they decompose in a short time - from several months to several years. Thus, the creation of compositions that along with the high molecular basis include organic fillers (starch, cellulose, amylose, amylopectin, dextrin, etc.), which are a nutrient medium for microorganisms is a promising trend in the packaging industry.

By the general structure, the majority of algae cells are similar to the cells of green plant such as corn or tomatoes; they have rigid cell wall, which consists primarily of cellulose, hemicellulose and pectins. Cellulose pulp, alkyl ketones and compounds containing carbonyl groups are the catalysts of photo and biodegradation of the films based on polyethylene, polypropylene, or polyethylene terephthalate. Photo and biodegradation of such films begins after 8-12 weeks, the remnants of the film completely disappear during harrowing and ploughing, thus loosening the soil.

The main commercial algae is brown algae, so this paper puts more emphasis on the representatives of this division. Brown algae (Phaeophycophyta) are spread exclusively in the seas; their appearance resembles the one of higher plants. Representatives of brown algae have a yellowish-brown colour of thalli, which is due to the presence of chlorophyll and carotenoids, as well as the brown pigment from the group of xanthophylls-fucoxanthine. Their vegetative body (thallus) is of complex internal and external structure. The thallus is composed of several types of tissues with different functions.

The chemical composition of brown algae is highly dependent on the species, season and habitat. According to the literature, brown algae contains from 2.5 to 17% of algal cellulose, which, due to certain differences from the usual, is called eucellulose[21].

Extraction of cellulose from natural materials is based on the action of reagents that solve or destruct non-cellulosic components contained in plant tissues (proteins, fats, waxes, resins, lignin and polysaccharides - cellulose companions). Extraction methods depend on the type of plant material and designation of cellulose. The main method is alkaline pulping - processing of plant materials with diluted sodium hydroxide solution. In the course of the research, we obtained the optimal technological parameters of the cellulose extraction process, thus allowing us to increase the yield of the final product.

The authors propose a new method for producing cellulose from non-wood cellulose-containing raw materials, which comprises the milling of dried raw material, delignification with dilute acid by heating followed by separation of the solid phase, which is treated with the aqueous solution of sodium hydroxide under heating, and then the desired product is filtered off, washed with water and dried.

An important advantage of the method proposed by the authors is the possibility to improve the sanitary condition of the coastline sections cluttered with deposits of cast ashore dry algae and improve the environmental situation in general. The study found that raw algal cellulose fibres are very small, in the shape of irregular flakes and dissolve in the Schweitzer reagent. Thus, sea algae is an ideal raw material for bio-packaging material.

3 Methodology

The method consists in the purification of large extraneous impurities of dried brown algae, mostly of the Fucus genus, followed by refinement through grinding and sifting. 4 to 6% solution of sulfuric acid (2SO4) is added to the sifted fine fraction with the 1: 45-55 hydromodule, and is heated at the boiling point of the mixture (100 to 105°C) for 5-10 minutes under reflux with continuous mechanical stirring. The reacted and cooled down mixture is filtered, and the mass precipitated on the filter is washed with hot water (60 to 70°C) until neutral and dried to constant weight. Then, 5-10% solution of the KOH alkali is added to the resulting solid residue, followed by hot distilled water (from 60 to 70°C) in equal amounts calculated to provide a hydro module of 1/50-60 at an alkali solution concentration of 2.5-5.0%, and it is heated at the boiling point of the mixture for 5-10 minutes with continuous mechanical stirring. The cooled mixture is filtered with it being rinsed with water as well. After complete filtration, the solid residue in the filter, which is the desired product, is washed and dried in natural conditions. After it is dried, it is in the form of brown powder, which goes into the reactions characteristics for cellulose: it is dissolved in Schweizer's reagent and forms a gelatinous cellulose mass if diluted acid is added to the resulting solution. Lignin-like residual content and other organic substances in the resulting product amounts to no more than 5-8 wt.%.

The proposed method differs from the known methods[22-25], as local sea brown algae is used as the non-wood cellulose raw material; at the same time, the delignification is carried out by heating in a 4-6% solution of sulfuric acid (S/L = 1/45-55) at the boiling point temperature of the mixture for 5-10 min; the alkaline treatment of the obtained solid residue is carried out after washing with water by heating in a 2.5-5.0% solution of potassium hydroxide KOH (S/L = 1/50-60) at the boiling point for 5-10 min.

Technological parameters of the proposed method ensure efficient processing of specific algal raw material with the product being based on cellulose, containing lignin residues (lignin-like substances) and trace content of other organic substances.

The conducted field tests showed that the resulting cellulosic semi-finished product acts as an effective filler of composite polymeric materials that serves as a nutrient medium for microorganisms, destroying high molecular basis, and can be successfully used in the production of various types of packages and containers with limited lifetime in particular.

For a more complete utilization of the algal mass and higher profitability the author suggest using acidic and alkaline filtrates for obtaining a valuable nutrient of the fertilizer, for this purpose, it is necessary to mix and separate them for the formation of the flocculated settling fraction, which is washed with water until neutral and dried.

Discussion. There are certain developments that envisage the use of different plant fillers as natural bio additives: flax waste, wheat stalks, corn stalks, wastes of sawmill and wood chemical industries, food production waste, etc. Today polymer blends are widely used (most often - polyethylene) with corn and starch, biodegradable polymers with natural additives - cellulose, soy flour, spent grains. The combination of a synthetic polymer and a natural material can give a new set of properties.

The authors studied the technical level in the sphere of development of the biodegradable additives into polymeric materials of a wide application range; a patent search is conducted, which revealed that many scientists, both in Russia and Europe mainly work in the field of biodegradable materials that are used as packaging materials[26-46].

From the perspective of rational environmental management as a natural supplement, it is feasible to consider the resources that one or another region is rich with. The fauna of the Far East is a rich source of unique plants. Algae make up the bulk of plant organisms in bodies of water and are the most productive plants. Large amounts of sea weed and algae are cast ashore in the Promorsky Krai; these plants contain fiber - plant cellulose, which, as the authors suggest, can be used as a natural filler for biodegradable composition.

It is the study on the degradation of algae that a large number of scientific papers and reviews are dedicated to [47-57]. By its general structure, most algae cells have similar cells to the cells of green plants such as corn or tomatoes. The studies have found that algae (cyanobacteria) are capable of synthesizing cellulose, which can be used as a biodegradable additive. The Far East is rich with brown algae, so in our work we focused on representatives of this division.

The chemical composition of brown algae is highly dependent on the species, season and habitat. It is found that brown algae contain up to 17% of algal cellulose, eu-cellulose, which is structurally similar to cellulose of higher plants, and thus it is a potential source[57]. The use of dry brown algae, which can be considered as non-wood cellulose waste, allows expanding the raw material base for producing cellulose, reduce the consumption of more valuable wood and get cheaper products due to the use of affordable renewable non-conventional raw materials.

Each plant contains cellulose, but not every plant is suitable for industrial extraction of cellulose. When choosing raw materials, the content of fibre is important, as well as structural features of the constituent cellular tissues, the possibility of using industrial processing methods, the quality of the product obtained as a result of this treatment, the prevalence of plant raw materials, cost of collection, storage.

Despite the proven similarity of the algal cellulose with the cellulose of higher plants in structure and properties, with the use of dry brown algae as cellulose-containing raw materials, the known cellulose production methods are ineffective and cannot exhibit sufficiently convincing results. The reason for this is that algal fibre contains lignin-like substances that are difficult to remove as they have strong bonds with it, as well as due to the residual amount of alginic acid, prone to certain conditions, to gel formation, and in some cases chlorophyll formation.

There is a known method for manufacturing cellulose powder from various kinds of lignocellulosic materials derived from wood semi-finished products in the course of their processing on the cellulose and paper plants, straw of herbaceous plants, waste paper (RF patent. No. 2478664, published on 2013.04.10) which includes the destruction of said materials via exposure to a Lewis acid solutions of low concentration and an organic solvent with stirring, followed by washing and drying of the desired product[24]. If there is a common idea consisting in the use of Lewis acids, this method includes unspecified number of variants, each of which requires an independent selection of optimum conditions for obtaining powdered cellulose: concentration values and the type of Lewis acid in various organic solvents, liquid module, temperature and a destructive treatment of the lignocellulosic material, the intensity of stirring and the conditions of drying of the end product, depending on the used raw material. Furthermore, cellulose production in the known manner on an industrial scale involves the use of substantial quantities of organic solvent, requiring certain safety precautions during handling and disposal. When this method is used for dry brown algae as a cellulose-containing raw material, it is ineffective and does not provide the production of the necessary target product.

There is a method of cellulose production from paddy straw (RF patent No. 2418122, published on 2011.05.10) comprising two pulping stages, the first of which is carried out in an alkaline medium with subsequent separation of the cellulose product, and the second-in an acidic environment, with a mixture of peracetic acid, acetic acid and hydrogen peroxide in the presence of a stabilizer, in this case, mixtures of organ ophosphonates, wherein second pulping stage is carried out in the presence of ozone at a rate of 2-4 g/hr[25]. The disadvantage of this method is the difficulty and cost of technology that are due to the need to conduct the process in the presence of ozone and due to the use of hydrogen peroxide, which is subject to rapid decomposition, and organic stabilizers. Furthermore, the known method is also ineffective when dry brown algae is used as raw cellulose-containing material.

There is a method of cellulose production from straw (RF patent No. 2423570, published on 2011.07.10) comprising impregnation in the reactor and maceration of chopped straw with the aqueous solution of sodium hydroxide with a concentration of 20-30g/l in Na_2O units at a temperature of 30-80°C at a ratio of the solution weight to the weight of dry chopped straw of 7:1[24]. The impregnated chopped straw is maintained at a predetermined temperature for 30 minutes, and then the liquid phase is withdrawn. Heated water is added to the mass, the mass temperature is raised to 96°C and the pulping is carried out at this temperature for 2 h 30 min. When used as a dry cellulosic raw material of brown algae containing non-hydrolysable substances strongly bonded with fibre and similar in elemental composition to lignins of higher plants, the known method is inefficient and does not provide a marketable product.

The closest to the claimed method is a methodof producing cellulose from non-wood plant raw material with the content of the native cellulose being not more than 50%, described in the RF patent No. 2448118, publ. on 2012.04.20[27]. According to the conventional method, the raw material is washed with water at 40-70°C and atmospheric pressure for 0.5-4 hours, and processing is carried out with an aqueous solution of nitric acid with a concentration of 2-8% at 90-95°C for 4-20h followed by separation of the solid phase, which is treated with the aqueous solution of sodium hydroxide with a concentration of 1-4% at 60-95°C for 1-6 hours. A disadvantage of this method is the long duration of the technological process, in addition, with the cellulose extraction from dry brown algae, the fibre of which contains lignin-like components and alginic acids that are hard to separate, it is possible to use the method with positive results and it does not provide an acceptable yield and quality of the end product due to the complexity of removing the tightly bound substances contained in algal cellulose and, on the one hand, and the partial hydrolysis of the fibre itself after prolonged treatment, on the other hand.

Result. Algae are a non-food biomass, the use of which does not pose a threat to the production of packaging and food safety. Algae grow 20-30 times faster than land plants (some species can double their mass several times a day). The lack of a hard shell and almost no lignin makes the processing technology easier and more efficient than biomass processing of any ground material.

It should be noted that the intensification of research in the field of polymers is important not only for further successful development of the market of biodegradable plastic packaging, but is one of the most promising ways to solve the global ecological problem related to the environmental pollution with polymeric materials wastes.

The proposal to use local raw materials as raw materials base can solve the problem of non-waste production in the industry. Among the possible priority areas we can note the development of ocean resources and the ecology, new technologies and materials. Today, modern biotechnology is aimed at the production of both traditional and new types of substances and materials. Moreover, at this point, renewable plant raw materials can become a solution to this problem, and the proposed technology for producing biodegradable additives for plastic packaging can be successfully used for the further industrial development in the Far East region of Russia.

The development presented in the article is an invention (patent No. 2556115 Russian Federation, IPC S08B15/02 (2006.01), appl. dated 15.04.14, published on 07.10.15), which relates to algae processing methods, in particular, of the sea brown algae cast ashore; this method can be used to produce fillers for synthetic polymersthat provide biodegradation of polymer compositions and are required for manufacturing materials with a controlled lifetime and to producecellulose semi-finished products used as raw materials for the chemical industry, in the manufacture of paper and cardboard.

Cellulose is not a product intended for direct consumption: cellulose obtained after a single technological cycle serves as a raw material for other processing cycle; varying degrees of cellulose purification determine its various applications.

An important advantage of the proposed method is the possibility to improve the sanitary condition of the coastline sectionscluttered with deposits of cast ashore dry algae and improve the environmental situation in general.

4 Conclusions

1. The technical result of the proposed method for producing the biodegradable additive from the Far East brown sea algae for plastic packaging is to reduce the duration of the technological process, increase the yield and quality of the end product and expand the resource base through the use of cheap and non-traditional local raw materials.

2. In the course of the research, we obtained the optimal technological parameters of the cellulose extraction process, thus allowing us to increase the yield of

the final product.

3. Technological parameters of the proposed method ensure efficient processing of specific algal raw material with the end product being based on cellulose, containing lignin residues (lignin-like substances) and trace content of other organic substances.

4. The resulting cellulosic semi-finished product acts as an effective filler for composite polymeric materials that serves as a nutrient medium for microorganisms, destroying high molecular basis, and can be successfully used in the production of various types of packages and containers with limited lifetime in particular.

5. During the study, the authors found that raw algal cellulose fibres are very small, in shape of irregular flakes and dissolve in the Schweitzer reagent. Thus, sea algae is an ideal raw material for bio-packaging material.

6. For a more complete utilization of the algal mass and higher profitability, we propose to use acidic and alkaline filtrates for obtaining a valuable nutrient of the fertilizer, for this purpose, it is necessary to mix and separate them for the formation of the flocculated settling fraction, which is washed with water until neutral and dried.

7. The novelty of the technological solution of cellulose production from brown sea algae is confirmed by RF patent No. 2556115 “The process for producing cellulose from brown sea algae”.

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References

[1] The Committee on Environment and Natural Resources. (2014), Available at: www.magas. bezformata.ru/listnews/tonn-tverdih-bitovih-othodov/23761174/.

[2] Perrin F.X., Merlatti C., Aragon E. and Margaillan A. (2009), “Degradation study of polymer coating: Improvement in coating weatherability testing and coating failure prediction”, *Progress in Organic Coatings*, Vol.64, No.4, pp.466-473.

[3] Eglin D., Mortisen D. and Alini M. (2009), “Degradation of synthetic polymeric scaffolds for bone and cartilage tissue repairs”, *Soft Matter* , Vol.5, No.5, pp.938-947.

[4] Ito M and Nagai K. (2008), “Degradation issues of polymer materials used in railway field”, *Polymer Degradation and Stability*, Vol.93, No.10, pp.1723-35.

[5] Lucas N, Bienaime C, Belloy C, Queneudec M, Silvestre F and Nava-Saucedo JE. (2008), “Polymer biodegradation: Mechanisms and estimation techniques”, *Chemosphere* , Vol.73, No.4, pp.429-442.

[6] Hakkarainen M. (2007), “Solid phase microextraction for analysis of polymer degradation products and additives ”,*Chromatography for Sustainable Polymeric Materials*, pp.23-50.

[7] Jorgensen M, Norrman K and Krebs FC. (2008), “Stability/degradation of polymer solar cells”, *Solar Energy Materials and Solar Cells*, Vol.97, No.7, pp.686-714.

[8] Borup R, Meyers J, Pivovar B, Kim YS, Mukundan R, Garland N et al. “Scientific aspects of polymer electrolyte fuel cell durability and degradation”, *Chemical Reviews*, Vol.107, No.10, pp.3904-51.

[9] Zeynalov E. and Friedrich J.F. (2007), “Anti-radical activity of fullerenes and carbon nanotubes in reactions of radical polymerization and polymer thermal/thermo-oxidative degradation”, *Materialprufung*, Vol.49, No.5, pp.265-270.

[10] Jayasekara R., Harding I., Bowater I. and Lonergan G. (2005), “Biodegradability of a selected range of polymers and polymer blends and standard methods for assessment of biodegradation”,*Journal of Polymers and the Environment* , Vol.13, No.3, pp.231-251.

[11] Gu JG and Gu JD. (2005), “Methods currently used in testing microbiological degradation and deterioration of a wide range of polymeric materials with various degree of degradability: A review”, *Journal of Polymers and the Environment*, Vol.13, No.1, pp.65-74.

[12] Kikkawa Y. and Doi Y. (2003) “Surface morphology and enzymatic degradation of biodegradable polymers”, *Sen-I Gakkaishi*, Vol.59, No.10, pp.313-318.

[13] Santovena A, Alvarez-Lorenzo C, Concheiro A, Llabres M and Farina JB. (2004), “Rheological properties of PLGA film-based implants: correlation with polymer degradation and SPf66 antimalaric synthetic peptide release”, *Biomaterials*, Vol.25, No.5, pp.925-931.

[14] Gu J.D. (2003), “Microbiological deterioration and degradation of synthetic polymeric materials: recent research advances”, *International Biodeterioration& Biodegradation*, Vol.52, No.2, pp.69-91.

[15] Lucarini M., Pedulli G.F. and Motyakin M.V. (2003), "Schlick S. Electron spin resonance imaging of polymer degradation and stabilization", *Progress in Polymer Science* , Vol.28, No.2, pp.331-340.

[16] Santerre JP, Shajii L. and Leung BW (2000), "Relation of dental composite formulations to their degradation and the release of hydrolyzed polymeric-resin-derived products", *Critical Reviews in Oral Biology & Medicine*,Vol. 12, pp.136-51.

[17] Wilkie CA(1999), "TGA/FTIR: an extremely useful technique for studying polymer degradation", *Polymer Degradation and Stability*,66:301-06,1999.

[18] "Degradation of polyethylene terephthalate (PET) by lignolytic fungi"(2000), *International Biodeterioration & Biodegradation*, Vol. 55, pp.308-09.

[19] Reiner CN. (2004), "Fluid catalytic cracking degradation of polyethylene terephthalate by various catalysts", *Abstracts of Papers of the American Chemical Society* ,Vol. 227,643-CHED, pp.119-135.

[20] Gijsman P, Meijers G and Vitarelli G. (1999), "Comparison of the UV-degradation chemistry of polypropylene, polyethylene, polyamide 6 and polybutylene terephthalate", *Polymer Degradation and Stability*, Vol 65, pp.433-41.

[21] *Cellulose and its derivatives* (1974), Bayklz N. and L. Segal.(Ed.), Mir.

[22] Pat. RU No2478664. (2013), "A method for producing cellulose powde", *Kuvshinov LA, Frolova SV, AV Kuchin, published* .

[23] Pat. RU No2418122(2011), A method for producing pulp from rice straw: Vurasko AV Driker BN, Mertin EV, Galimov AR, Chistyakov KN, publ.

[24] Pat. RU No2423570(2011), A method for producing pulp from straw: Pazukhin GA, Moncef Sh.R., publ.

[25] Pat. RU No2448118(2012), A method for producing pulp from non-wood plant raw material with the content of the native cellulose is not more than 50% and a method for producing therefrom carboxymethylcellulose, publ.

[26] Pat. RU No 2352597(2008) biodegradable granular polyolefin composition and method of preparation. Alexander Ponomarev, T-ka No 2008125461/04, Priority 2008.06.25, publ. 2009.04.20.32.; Pat. RU No 2114865 Biodegradable crosslinked polimery.Nikomed Imaging AS not (NO). 3. No94045151 / 04, Priority 1992.03.06, publ. 1998.07.10..

[27] Pat. RU No 2114865(1992) Biodegradable crosslinked polimery.Nikomed Imaging AS not (NO). 3. No94045151 / 04, Priority 1992.03.06, publ. 1998.07.10.

[28] Pat. RU No 2095379(1992) Polymer composition for producing biodegradable moldings and biodegradable moldings NovamontS.p.A. (IT). 3. No 92016573/04, priority 04.05.1992, publ. 10.11.1997.

[29] Pat. RU No RU 2174132(2000) Production of plastics based on natural polymers used in the production of thermoformed articles of various configurations. Moscow State University of Applied Biotechnology, W-ka No 2000116003/04, priority 23.06.2000, publ. 27.09.2001.

[30] Pat. RU No 2180670(2000) Biodegradable thermoplastic composition based krahmala.Vserossiysky Research Institute starch, T-ka No 2000100058/04, priority 06.01.2000, publ. 20.03.2002.

[31] Pat. Number RU 2349612(2007) a biodegradable thermoplastic composition using the waste confectionery. State Educational Institution of Higher Professional Education "Moscow State University of Food Production", Ministry of Education of the Russian Federation, the W-ka No2007141897 / 04, priority 14.11.2007, publ. 20.03.2009.

[32] Pat. S No ES2315533(2002) Water-solublecontainerobristclosuresswitzerland, Z-KA ES20030762682T, submitted 2003.06.26 Priority 2002.07.03, published. 2009-04-01.

[33] Pat. Britain No GB 2452227(2007) PackagingmaterialsportabrandsLTD. Z-KA No GB20080009345, submitted 2008.05.23 Priority 2007.08.28, published. 2009-03-04.

[34] Pat. Korea No KR20000005282(2006) Water-soluble bag packaging system and packaging method Novartis AG [CH]; Chris chraftind products INC [US]. Z-KA No KR19987007990 submitted 1998.10.08, Priority 1996.04.08, published. 2000-01-25.

[35] Pat. France No FR2691467(1993) Hot water soluble saccharide based sheet material for thermo-forming rigidpackaging containers - comprises starch based saccharide, alkali salt of proteinaceous material, organic plasticiser and water gervaisdanone SA. Z-KA No FR19920006279, Submitted 1992.05.22, published. 1993-11-26.

[36] Pat. UNITED STATES No US7402618(2006) Biodegradable composition for the preparation of tableware, drink container, mulching film and package and

method for preparing the sameXu; Hao Z-KA No 11/418,628, Submitted May 6, 2006, published. July 22, 2008.

[37] Pat. UNITED STATES No US7368160(2005) Packaging film Biax International Inc.CA Z-KA No 11/142,296, Submitted June 2, 2005, published. May 6, 2008.

[38] Pat. UNITED STATES No 7288196(2005) Packagingmaterialandinformation recording by packaging informationrecording media packaged by packaging material.Science Applications International Corporation CA. Z-KA No 11/101,441, Submitted April 8, 2005, published. October 30, 2007/.

[39] Pat. UNITED STATES No 71324637(2003) Biodegradable composition having improved water resistance and process for producing sameYoul Chon Chemical Co., Ltd.KR. Z-KA No 10/490,671 Submitted June 9, 2003, PCT Filed June 09, 2003 PCT No.: PCT/KR03/01120, published. November 7, 2006.

[40] Pat. UNITED STATES No 7083673(2004)Biodegradable or compostable containers New Ice LimitedGB- No10/977,082, Submitted October 29, 2004, published August 1, 2006.

[41] Pat. UNITED STATES No 706765(2002) Non-synthetic biodegradablestarch-based composition for production of shaped bodiesKasetsart University, Bangkok, TH Z-KA No 10/282,205, Submitted October 29, 2002, published. June 27, 2006.

[42] Pat. UNITED STATES No 6878199(2003) Biodegradable orcompostablecontainersNew Ice Limited (GB) Z-KA No 10/341,288, Submitted January 13, 2003, published. April 12, 2005.

[43] Pat. UNITED STATES No 6723264(1997) Method of making biodegradablepackaging material Bussey, Jr.; Harry (FL), Bussey, III; Buddy Harry (NJ) Z-KA No 08/867,771, Submitted June 2, 1997, published April 20, 2004.

[44] Pat. UNITED STATES No 6706684(2001) Method for preparing a collagen material with controlled in vivo degradation ImedexBiomateriaux,Trevoux, FR. Z-KA No09/856,858, Submitted May 29, 2001, PCT Filed November 09, 1999 , published. March 16, 2004.

[45] Pat. UNITED STATES No 6573340(2003) Biodegradable polymer films and sheets suitable for use as laminate coatings as well as wraps and otherpackagingmaterials.BiotecBiologischeNaturverpackungen GmbH & Co. KG (DE) Z-KA No 09/648,471.Submitted09/648,471, published. June 3, 2003.

[46] Pat. UNITED STATES No 6337097(2002) Biodegradable and edible feed packaging materialsKansas State University Research Foundation (Manhattan, KS). Z-KA No09/408,373 SubmittedSeptember 29, 1999, published. January 8, 2002.

[47] Caceres TP, Megharaj M and Naidu R. (2008), "Biodegradation of the Pesticide Fenamiphos by Ten Different Species of Green Algae and Cyanobacteria", *Current Microbiology*, Vol. 57, pp.643-46.

[48] Warshawsky D, Ladow K and Schneider J. (2007), "Enhanced degradation of benzo[a]pyrene by Mycobacterium sp in conjunction with green alga", *Chemosphere*, Vol. 69, pp.500-506.

[49] Alderkamp AC, van Rijssel M and Bolhuis H. (2007), "Characterization of marine bacteria and the activity of their enzyme systems involved in degradation of the algal storage glucanlaminarin", *Fems Microbiology Ecology*, Vol. 59, pp.108-117.

[50] Zhou C.S. and Ma H.L. (2006), "Ultrasonic degradation of polysaccharide from a red algae (Porphyrayezoensis)", *Journal of Agricultural and Food Chemistry*, Vol. 54, pp.2223-2228.

[51] Meneses C.G.R, Saraiva L.B., Mello HND., de Melo JLS and Pearson HW. (2005), "Variations in BOD, algal biomass and organic matter biodegradation constants in a wind-mixed tropical facultative waste stabilization pond", *Water Science and Technology*, Vol. 51, pp.183-190.

[52] Hirooka T., Nagase H., Uchida K., Hiroshige Y., Ehara Y., Nishikawa J. et al. (2005), "Biodegradation of bisphenol a and disappearance of its estrogenic activity by the green alga Chlorella fusca var", *vacuolata. Environmental Toxicology and Chemistry*, Vol. 24, pp.1896-1901.

[53] Michel G., Helbert W., Kahn R., Dideberg O. and Kloareg B. (2003), "The structural bases of the processive degradation of iota-carrageenan, a main cell wall polysaccharide of red algae", *Journal of Molecular Biology*, Vol. 334, pp.421-433.

[54] Regel R.H., Ferris J.M., Ganf G.G. and Brookes J.D. (2002), "Algal esterase activity as a biomeasure of environmental degradation in a freshwater creek", *Aquatic Toxicology*, Vol. 59, pp.209-223.

[55] Ding HB and Sun MY. (2002), "Biodegradation of algal fatty acids in oxic and anoxic systems: Effect of structural association and relative roles of aerobic and anaerobic bacteria", *Abstracts of Papers of the American Chemical Society*, Vol. 223, 067-FUEL.

[56] Ivanova E.P., Bakunina I.Y., Sawabe T., Hayashi K., Alexeeva Y.V., Zhukova N.V. et al .(2002), "Two species of culturable bacteria associated with degradation of brown algae Fucusevanescens", *MicrobialEcology*, Vol. 43, pp.242-249.

[57] Avakova O.G. and Bogolitsyn K.G. (2004), "Vegetable fiber: structure, proper-ties, applications". Publishing house: University, *Forestry Journal*, No. 4.C, pp.122-129.

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