In: Polymers, Polymer Blends, Polymer Composites… ISBN 1-60021-168-2
Eds: A.K. Mikitaev, M.K. Ligidov et al., pp.183-185

Chapter 25

RECEPTION AND RESEARCH OF THE PROPERTIES OF MODIFIED STARCH

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ABSTRACT

The technologies of producing starch at the open joint-stock company «KST» (KBR, Maiskiy region, village Aleksandrovskaya). The characteristics of 3 kinds modified starch are given. The use of modified starch for receiving biodecomposable packing materials is studied.

Keywords: starch, biodecomposable polymer.

Starch is the most widely used material of all the natural compounds of biodecomposed packing materials.

Starch, as is it known, is the most widespread material of plants. Starch is formed in leaves of plants as a result of photosynthesis and is postponed in roots, tubers and seeds as grains. In industrial conditions starch is received from potato and corn. Starch of wheat, rice, sorghum and other plants has less industrial value. The production technology of starch depends on the kind of raw material and the purposes for which the starch is made.

The open joint-stock company "KSF" (KBR, Maiskiy region, village Aleksandrovskaya) 3 kinds of modified starch are produced now:

1) Starch modified for drilling.
2) Starchite.
3) Swelling food starch.

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The reception of modified starches is carried out on the Dutch rolling dryers which are warmed with steam at a certain pressure. Starch suspension of a certain density is moved on a drum rolling dryers and, having turned to paste, is dried up in a thin layer. The received film is cleaned off by a knife and goes into the crusher where through the certain apertures in the grid it is blown into the bunker to be packed in bags.

Swelling food starches that passed water and thermal treatment, get new structure, i.e. there is a splitting of polysacharide starch grains.

Received split starches have ability to swell in cold water and pass completely or partially into a soluble condition.

The technology of releasing these three kinds of modified starch is practically identical and depends only on the density of starch suspensions, chemical additives and the grid of prosowing.

1) "Starch modified for drilling" is a technical starch. For its reception into the starch suspension of 40 % C.B. salt – oxidizer and alumokaly alum $(KAl(SO_4)_2) \cdot {}_{12H_2O}$ are added, then mixed in the reactor and submitted on rolling dryer. The received film goes to a crusher with diameter of a grid 4 mm. This starch is applied as the stabilizer of clay solutions at drilling chinks in gas and a petroleum-refining industry.
2) "Starchite" is a technical starch. It is developed on the same technology, without additives, but with the increased density starch suspensions up to 42-44 % C.B. with the diameter of the cell of the grid being 5 mm. "Starchite" is applied in the foundry industry as a forming material while manufacturing pastes, i.e. it is used as a softener and holder of superfluous moisture of forming mixes at work on automatic transfer lines for casting blocks of automobile engines.
3) "Swelling food starch" is a food starch. It is developed also without additives, but with the density of starch suspensions lowered up to 36-38 % C.B. and prosowing through a sieve with diameter of a cell of 3 mm. This starch is applied in the various food-producing industries as an additive to condense mayonnaise, ketchup, tomato paste, jam, ice-cream, etc., it is also used to improve the quality of flour instead of gluten (5 kilos per 1 ton of flour). This starch is used for producing puddings of fast preparation, for producing protein-free food stuffs as bread, macaroni, etc. It is also widely used for briquetting forage; agglomeration of various products such as powder, ores, coal, etc.

The quality of these three kinds of modified starch is according to their ability of swelling, holding of superfluous moisture and stabilizing ability of viscosity and solubility and is regulated by specifications on each kind of production.

The simultaneous application of softeners and glycerin allows to receive flexible thermoplastics of starch using compressive pressing [2] and extrusion [3].

The materials received from corn, potato and wheat starch, containing constant in relation to starch quantityof glycerin (1:0,3) and from 8 up to 25 мас. % of water, were elastic, i.e. had T_c below 20 C . While researching mechanical properties of such materials the dependence of the module of elasticity of an explosive pressure of samples not only on the contents of the softeners, but also on the nature of the starch was found out. In the opinion of the authors of the work [3], the reason of difference of mechanical properties can be caused

by the big maintenance of amylopectin in the corn starch which is better masticated with water, than potato starch enriched with high-molecular amylose.

On the of the invention [4] we received samples destroyed starch containing 80 % starchite, 1 %, hydrogenated fat and 18 % of water. After preparation the mixture has the form of a loose powder. The received mixture is loaded into the plodder, in the auger cylinder (temperature ≈160-170 C) the given powder fuses. Then the fusion is pressed through and divided into grains with average diameter 2,5-3,0 mm. The material has a form of a firm white product with thin foamlike structure. With the received material it is possible to press test samples, suitable for studying their properties. The durability and flexibility of the received samples can be noted. It should be noted, that if to press test samples at once from the prepared composition they turn out to be more fragile.

Besides glycerin and polyglycols, plasticizing effect on starch has such substances as sorbite, natrium salt of dairy acid, urea, ethylene-, diethylene-, polyethyleneglycol and diacetate glycerin. [5]

Water used in extrusion starch does not only transfer the system into the thermoplastic condition, but also partially protects the polymer from destruction. Addition of water and others hydroxide-containing substances are used for disposable or not long-term application. In this connection mixes of starch with synthetic polymers get the increasing value. These materials combine properties of the synthetic component present in them and have the ability of biodegradation due to the presence of a natural biodecomposed component - starch in the system [6-9]. It is necessary to note, that biodecomposition of films with similar structures (on method astm-d-5209-92) occurs actively with allocation of $_{co2}$, microbiological weights and the metabolic products useful to plants [7].

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In: Polymers, Polymer Blends, Polymer Composites… ISBN 1-60021-168-2
Eds: A.K. Mikitaev, M.K. Ligidov et al., pp.187-191

Chapter 26

BIOLOGICALLY UTILIZED PLASTICS: CONDITION AND PROSPECTS

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ABSTRACT

The survey of literary sources devoted to the problem of creation of biologically utilizable plastics. In the sake of creating biodecomposable materials the researchers turned to various of row material of both synthetic and natural origin. Ecological consequences of introduction of biodecomposable polymers are considered.

Keywords: survey of literary, biodecomposable materials, Ecological consequences.

The packing material, polymeric film, polythene (polyolefins, ethylene copolymers, etc.) have received such a wide application, that neither human activity, nor, all the more, natural environment is capable to cope with the inflow of polymeric waste products. In this connection there appeared a necessity of manufacturing of polymeric materials capable of biodecomposition under the influence of the environment and microorganisms.

Now there is a lot of such developments and ideas of creation of such polymeric materials, but they either are insufficiently developed, or are not effective in the economic way.

For creation of high-quality and economic bioplastics researchers turned to various sources of raw material, such, as corn starch, capola, castor oil, soya fiber and so on. Plastics polyols on the basis of soy bean used for carpet coverings are already developed and produced now. Technologies for producing bioplastics on the basis of soy oil, and also new

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biotechnologies with application of fermentative processes with the purpose of use of animal fats, vegetable oils and industrial wastes are developed [1].

The current situation on development and mastering of biodecomposed polymers is given estimation and three basic directions in this area are allocated: ПЭФ hydroxide carbonic acids (glycollic, dairy, valerianic), plastics on the basis of reproduced natural polymers (water-soluble ПЛ from a mix of starch and pectin, and also a mix of starch from PVC, ПВС, compositions are actively developed on the basis of cellulose, chitin), giving biodecompositionability to industrial high-molecular synthetic materials (ПЭ, software, PVC, ПС, ПЭТФ). Now three directions of giving biodecompositionability to large-tonnage polymers are developed: getting of compositions with biodecomposed natural additives (compositions ПЭ with starch, etc. Biodecomposed additives), the directed synthesis of biodecomposed plastics on the basis of industrially - mastered synthetic products (synthesis corresponding ПЭФ and polyetheramides), introducing into the structure of biodecomposed polymers of the molecules containing in their structure functional groups, promoting the accelerated photodecomposition of polymer (СПЛ ethylene with carbon oxide, introduction of vinylcetone monomer as СПЛ ethylene or styrene, introduction in ON dithiocarbamic iron, nickel or corresponding heroxides, and also introduction of a pulp of cellulose, alkylcetones or fragments containing carbonyl groups) [2].

SYNTHETIC POLYMERS

Most frequently starch is used to modify polythene (ПЭ) - a film material which is usually used for short-term application. Thermo-softening mixes of synthetic polymer with starch are received by using, as a rule, starch, plasticized glycerin and water. Biodecomposition is promoted usually by use of additives of small quantities of prooxidizers. For example, such composition is: ПЭ - starch - vegetable oil. [3]

At the 16 congress by D.I.Mendeleyev .I.Suvorova and research assistants presented a biodecomposed mix of starch and synthetic polymer. The biodecomposed materials received on the basis of renewed raw material were presented. The properties of mixes of starch with hydroxypropyl-, carboxymethyl-and methyl - Ц, polyethyleneoxides and copolyamides. The sorbtion and diffusion of water steam and absorption of water in such materials were investigated defined. Properties of the materials were investigated by ГХ methods with detecting on heat conductivity at using He as the carrier. The speed of biodecomposition was defined according to the speed of allocation $_{CO2}$, the dependence of biodecompositionability from the maintenance of starch in the material was investigated [4].

For the convenience of mulching the films are received from polyolefin introducing into the composition of photosensitive additives - iron and nickel dithiocarbamat or corresponding heroxides. With the purpose of acceleration biodecomposition of films on the basis of polythene for an agriculture, polypropylene pulp of cellulose is put into them [5].

Cellulose, starch, polyethers in this case are a source of a nutrient medium for microorganisms due to that there is an almost compete biodecomposition.

But these development are insufficiently effective, as synthetic polymers are exposed to biodecomposition very badly.

In this connection new technologies of creation of biodecomposed polymers were developed, these are polymers are of a natural origin, such as pectin, cellulose, starch and others. With addition in KM chitosan ПЛ with improved superficial properties at preservation of ability to biodecomposition is received. It is shown, that when composting destruction of ПВС begins. [5, 6].

POLYMERS OF A NATURAL ORIGIN

Plastics of soy protein and corn starch, made by various methods, are investigated on bio destroyability on kinetics of CO2 allocation. Molded materials made of them are exposed to biodecomposition faster than raw materials. This effect is charged due to denaturation of protein and gelatinization of starch. At reception of plastics soy protein, corn starch, softeners were mixed and samples were mould.

In 2003 in Vladimir at the scientific and technical conference the material of creation biodecomposed film nanoaggregate on the basis of cellulose and starch were presented. Liquid nanoaggregate solutions of cellulose in MMO represent discrete box-cover structures of clay into the interbatch spaces which macromolecules of cellulose forming with a polymeric matrix labile structural associates are included. The revealed structural transformations predetermine also the operational properties of nanoaggregate films on the basis of cellulose, starch and natural, layered silicates. Introduction of starch into the cellulose solutions allows to receive a new film material with more than 4 times increased, in comparison with cellulose films, moisture-holding properties [5].

The compositions (KM) containing starch (KP), polyvinyl spirit (ПВС) and glycerin cast from a solution in the SQUARE. At composting ПЛ within 45 day KP and glycerin completely decay, whereas ПВС remains basically not destroyed. ПЛ from KM with maintenance of ПВС of 20 % are determined as having required physical characteristics at maintenance of KP in quantities sufficient for biodecomposition. While adding chitosan into KM ПЛ with the improved superficial properties at preservation of ability to biodecomposition is received [6].

At the IX All-Russia student's scientific conference devoted to the 130-anniversary of opening of D.I.Mendeleyev’s Periodic law in Ekaterinburg, the report on phase division in a biodecomposed mix of starch and polymer with vinyl acetate was presented. [7]

With the method of hot formation under pressure films of mixes of starch with a сэвиленом-copolymer vinyl acetate (BA) with various maintenance of BA in a copolymer (from 5 up to 25 %). are received. With the help of water sorbtion in a liquid phase it is revealed, that with the increase of maintenance ofBA in the mixture water absorption increases. The method of points of turbidity phase diagrams of mixes are received and is shown, that with the increase of maintenance of BA in the system miscibility of сэвилена with starch improves. Biodegradability was estimated with the method of gas chromatography by comparison of speed of allocation of carbonic gas at biodegradation films in watersoil suspension. It is revealed, that speed of biodegradation grows at the increase of maintenance of starch in a polymeric composition. The received data allow to choose optimum structure of components of the investigated mixes, providing good operational properties and ability to biodecomposition [7, 11].

The world's largest factory producing packings for foodstuff by a method of polymerization of a dairy acid of 140 thousand ton per year , plastics biologically was started in operation in the USA. Films from a mix of corn starch and a polymeric dairy acid, extruded corn flour etc. can be used as a material for manufacturing such packings as well. It is marked, that these materials are similar to synthetic polymers. The firms which produce the given materials are listed, and it is pointed, that the basic lack of these materials is their high cost which more than 2 times exceeds the cost of polystyrene and polypropylene, and in the USA and Europe factories producing new packing materials biologically decomposed after using according to their purpose have already been started.[8].

Firms Petroplast AG and Vinora AG (both in Switzerland) are engaged intensively in the search of packing materials which are alternatives to polythene and are destroyed biologically. To this materials belong those grown from raw material, first of all on the basis of corn starch - CompoBag with use of product Mater-Bi of firm Novamont belonging to chemical group Montedison (Italy). This product is processed, as well as traditional polymers, is painted biologically destroyed by uterus mixes or natural pigments, thermally vignetted on a paper, cardboard, a cotton and other natural fabrics, is antistatic, is sterilized and sticked together with traditional glues. Some types Mater-Bi can be used while producing packing materials for food stuffs [9].

ECOLOGICAL CONSEQUENCES OF INTRODUCTION OF BIODECOMPOSED POLYMERS

There is an assumption in the literature, that biodecomposed polymers brought into ground can negatively influence the growth of plants. Therefore biodecomposition of starch (КХР), straw, polyhydroxybutyrate, polylactide and thermally processed and mixed ПЭ up to a biomass and $_{CO2}$, and also their influence on the growth of watercress (КС) and millet is investigated in the work. The change of pH, volatility, breath of the ground, the maintenance of metals were studied. Insignificant influence КХР on the growth of plants, strong microbiological decomposition of straw without chemical-toxic separations with some initial delay of growth of КС is established. Some biodecomposed polymers cause insignificant delay of growth, but then it is normalized. It is established, that there is no observed connections between change of concentration of ions, pH-quantities with the factor of the slowed down growth of plants; the process has no chemical basis [10].

To sum up, it is necessary to note, that yet we can not do without polymeric materials which are in the lead on the degree of environmental contamination, but using traditional plastics means ignoring the fact, that after any processing they sooner or later appear garbage with which neither people, nor nature can do anything. Therefore only the use of decomposable polymeric materials is the reasonable alternative in preservation both the planet and health of its inhabitants.

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In: Polymers, Polymer Blends, Polymer Composites… ISBN 1-60021-168-2
Eds: A.K. Mikitaev, M.K. Ligidov et al., pp.193-195

Chapter 27

COMPOSITE MATERIALS CAPABLE OF MULTIPLE PROCESSING (ECOLOGICAL ASPECTS OF THE PROBLEM)

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At the end of the 20th century, which is often called as the century of polymers, we can be firmly convinced that the future of the national economy will be defined by creating and using new materials. Possessing the set of valuable characteristics such as high durability, little weight, flexibility, specific electrical properties, chemical stability, to the fast and mass production and processing into the items of complicated form and different colours the polymers took the first place practically in all branches of production.

However expansions of production and use of polymeric materials raised before mankind a problem of placing their wastes and repeated use of worked plastic materials. In Russia this problem hasn't been discussed though the struggle for keeping the Earth from littering plastic wastes is going on all over the world. The rational ways of using of polymeric wastes is constantly being developed.

It is known that the information is growing at least twice as fast that industrial potential. Nowadays more that 10.000 of periodical editions reflecting the ecological themes are appeared in the world. A number of organizations examining these problems several times as much. That is why one of the important tasks is the realization of information support of ecological researches (particularly the researching in the field of polymeric wastes utilization).

At present there are 4 trends of process of the plastic wastes utilization:

1) Recycle in materials.
2) Chemical way to the getting original raw materials and pyrolysis.
3) Burying of biodegradable polymers.

4) Burning.

The creation of such polymeric materials which are capable of multiple processing, reserving at high level exploiting characteristics is considered to be a base of successful realization of material recycle of polymeric wastes.

Polydefins particularly polyethylene of high density (HDPE) belong to the class of thermoplastics which can be used in the various fields of engineering. Every day tons of polymers all over the country are thrown away as waste products (mainly wrappings and packaging). It is known that polyethylene can pollute the environment without biodestruction for a long time. That is why the examining of high-density polyethylene utilization problem is guite actual. With that purpose we were examining the molecular weight change (M_w) of with the multiple extrudering (n=1-5), and also the character of phosphoroorganic polymer influence on the molecular weight of polyethylene.

As it is known, polymers are not used without addional stabilization. As polyolefin's stabilizers particularly for HDPE various phenols with tretbutul substitutes are often used. One of them is Irganox-1010 (Swiss production). In this connection one of purposes of our testing was the comparison of influence character of phosphoroorganic polymer and Irganox-1010 on M_w change with multiple processing of HDPE.

Phosphoroorganic polymers synthesized by low temperatured acceptor-catalyst polycondensation of diphenilolpropane with methyldichlorphosphanate and has viscosity 0,4дл/г (dichlorethane; T=293K; c = 0,5 г/дл.

The compositions of polyethylene with phosphoroorganic polymer (0,05 - 0,5%) were prepared by the method of exstruding the blend of initial components (T= 473K; 10 - 12 об/мин; the length of heating part of extruder is 22см)

Melt index, characterizing rheological properties of polymer melts for HDPE and compositions on its base were determined (IIRT-M type) at 463K and2,16 and21,6 kg Load (Russian normative quality document 11645-73), and calculating was done by the following formule:

$$ПТР=(m_{ср}\times\tau_0)/\tau ,$$

where ПТР-melt index;

τ_0=600c-standart testing time for polyethylene;

τ -time of melt outflow in the experiment;

$m_{ср}$= average weight of three measurements.

The values of M_w (molecular weight), M_n (molecular-mass distribution) were calculating on the base of melt index data using known ratio for HDPE:

$$\lg M_w = \lg 129000 - 0{,}263\times\lg ПТР_{2{,}16}^{463}$$

$$\lg (M_w/M_n)=\lg 0{,}0275+1{,}4\times\lg (ПТР_{2{,}16}^{463} \big/ ПТР_{21{,}6}^{463}),$$

where $ПТР_{2{,}16}^{463}$ - melt index value at 463K and 2,16kg load

$ПТР_{2,16}^{463}$ - melt index value at 463K and 21,6kg load.

Usually (M_n) value characterizes alow-molecular part of (MMD), and (M_w) value characterizes a high- molecular part of (MMD) it is determined that M_w HDPE increases from 269000 till 303000 after single extruding and falls down to 214000 ofter quintuple extruding. Addaning phosphoroorganic polymer in quantity 0,5 allows to kup molecular mass of HDPE practically at the same level (295000) despite extruding division (up to 5 times). Industrial polyolefin stabilizer Irganox-1010 maintais M_w HDPE within the limits 245000-257000. It is necessary to emphasize that the presence of phosphoroorganic polymer in polyethylene makes the polymer fireproof better.

These results of testing tell us about the perspective using of phosphoroorganic polymer stabilizer and modifier during the utilization of wastes of nigh density polyethylene.

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