Chapter 14

RADIATION MODIFICATION OF POLYSACCHARIDES AND THEIR COMPOSITES/NANOCOMPOSITES

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1. INTRODUCTION

The trends to replace environmentally non-degradable polymers made from feedstocks based on petroleum or natural gas and to invent new products for biomedicine, and food or pharmaceutical industries, *etc.*, have spurred the development of materials derived from renewable resources. These natural materials should be more environmentally friendly, but require different processes and, in some cases, different manufacturing techniques. Polysaccharides are a large family of such natural polymers and have been extensively studied. The following are some areas of interest in pursuing these natural polymers:

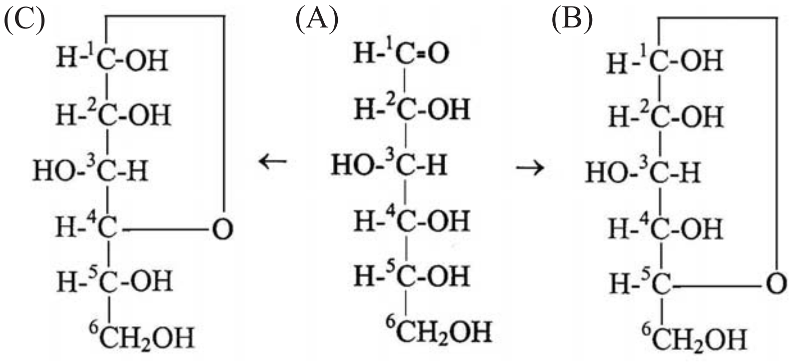
- natural polysaccharides produced by extraction from plant and animal tissues, and the derivatives of polysaccharides;
- products, by-products and wastes from agriculture and the food or paper industries (*i.e.* flours, bleached wood pulp, sugar cane bagasse, wheat straw);
- composites based on several polysaccharides or on polysaccharide-protein, polysaccharide-biodegradable synthetic polymers, polysaccharide-polyolefin and/or such containing some plasticizers, inorganic compounds (*i.e.* clays, TiO_2, SiO_2), lipids and surfactants;
- nanopolysaccharides and nanocomposites containing the above-mentioned polysaccharides and the addition of nanoparticles, such as inorganic nanoparticles (*i.e.* nanoclays, nanooxides, nanosilver), carbon or polymer/biopolymer nanoparticles, and all composites containing nanopolysaccharides.

Appropriate modifications of polysaccharides are done, often on an industrial scale, but using chemical, enzymatic or physical treatment to adjust properties for a given application. However, chemical processes rely on strong chemicals, while enzymatic methods can be rather expensive. Besides modifying the bulk polymer, surface modification can be conducted.

There has been increased interest in the use of radiation (*i.e.* ultraviolet radiation (UV), gamma or X-ray photons and fast electrons) in processing and modifying polysaccharides.

2. STRUCTURAL PROPERTIES OF POLYSACCHARIDES

The most common polysaccharides are: starch, cellulose and hemicelluloses, agar-agar, alginates, carrageenans, chitin and chitosan, pectin, and various plant gums. Although not a polysaccharide, lignin is a natural polymer that accompanies to celluloses in plant cells. Lignin is composed of three aromatic alcohols, whose structure determine the strong resistance of lignin to physical and chemical treatment.



Scheme 1. Fisher projections of aldoses: D-glucose (A), α-D-glucopyranose (B) and α-D-glucofuranose (C).

Polysaccharides are formed by monosaccharide units (Scheme 1) bonded by glyosidic linkages, as shown in Figs.1 and 2. There are a great number of

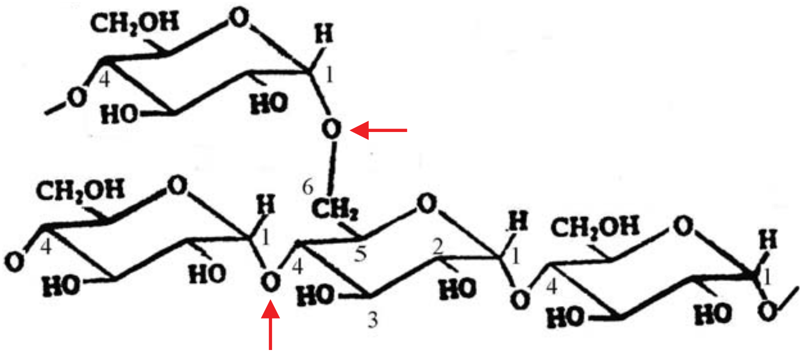


Fig.1. The structure of the starch amylopectin molecule (α-D-glucose unit, α1–4 and α1–6 linkages) with the most possible reaction paths (shown by the arrows). Starch amylose (non-branched) is formed by α-D-glucose units bound by α1–4 linkages.

possible monosaccharides differing in the molecular structure and conformation. Aldoses or ketoses (polyhydroxy aldehydes and polyhydroxy ketones) can be distinguished by their dependence on the position of C=O linkages in the molecule. An example of aldose is given in Scheme 1. Each saccharide can form several cyclic structures, as illustrated by the conformations B and C in Scheme 1. The positions of the OH groups at C1 and C2 in relation to the plane of the ring structure (*cis* or *trans*) are denoted as the α and β forms. The molecules can take the chair conformation (preferred in a majority of monosaccharides, as shown in Figs.1 and 2), or a twisted-boat conformation.

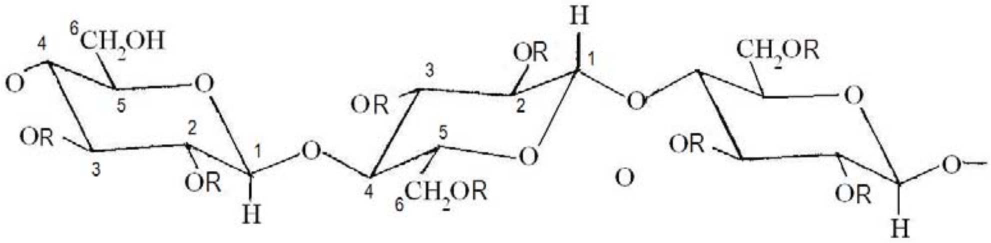


Fig.2. The structure of cellulose molecule (α-D-glucose unit, β1–4 linkages) or the ether and ester derivative of cellulose. Cellulose R = H, ether: R = H or CH_3 (methyl cellulose, MC), CH_2CH_2OH (hydroxyethylcellulose, HEC), *etc*. Ester: R = H or residue of carboxyl acid salt (*i.e.* $CH_2COO^-Na^+$ in the case of carboxymethylcellulose, CMC).

Polysaccharides can be composed of one type of the monosaccharide structural unit (homoglycans) or of several different types of structural units (heteroglycans) [1]. These can be connected by various types of glycosidic linkages, such as *1→4, 1→3, 1→6, 1→2,* as illustrated in Fig.1. Different functional groups, as COO^-, SO_3^-, $-NHCOCH_3$, NH_2^- in alginates, in carrageenans, in chitin and in chitosan, can substitute for the OH groups in the sugar units at different positions. These substitutions affect the conformation of the particular structural units of a polysaccharide. The presence of several types of the glycosidic linkages within the same polysaccharide may result in the formation of a branched molecule, as shown in Fig.1.

Accordingly, the structure/conformation of a polysaccharide macromolecule depends on all of the above factors. The most common conformations are the ribbon types (typical in cellulose fibers or alginates), the helix types (single or coiled double or triple helices; double helices are typical for starch) and the egg-box types (alginates stabilized by the Ca^{2+} ions). The ordered distribution of the chains results in the formation of ordered regions in the polysaccharide fibers or grains.

A great variety of possible polysaccharide structural types leads to a great variety of physical properties and of potential reactivity. The most important general physical property of all polysaccharides is their ability to capture water which results in the formation of hydrogels in aqueous environments. This can be achieved by heating a polysaccharide suspension, as for starch gelatinization, or by directly immersing a polysaccharide in water, as to swell agar-agar. This property determines numerous uses of polysaccharides as food hydrocolloids, in biomedicine, in technical industries and in environmental protection.

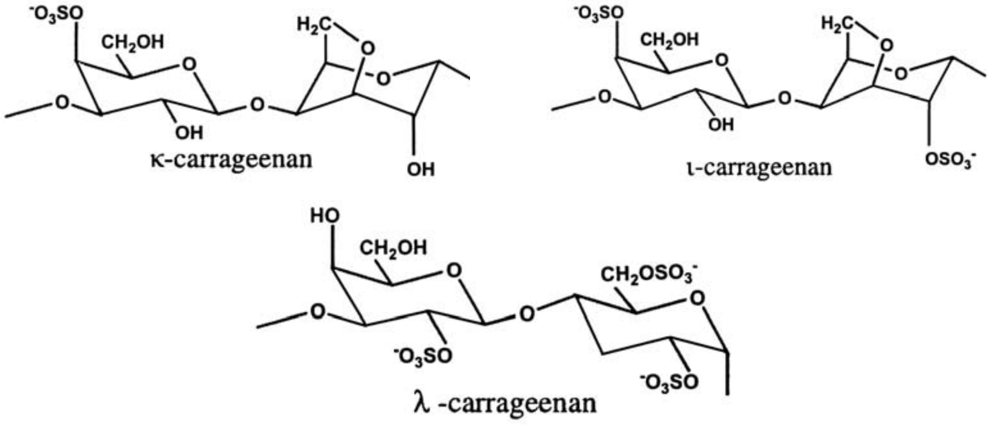


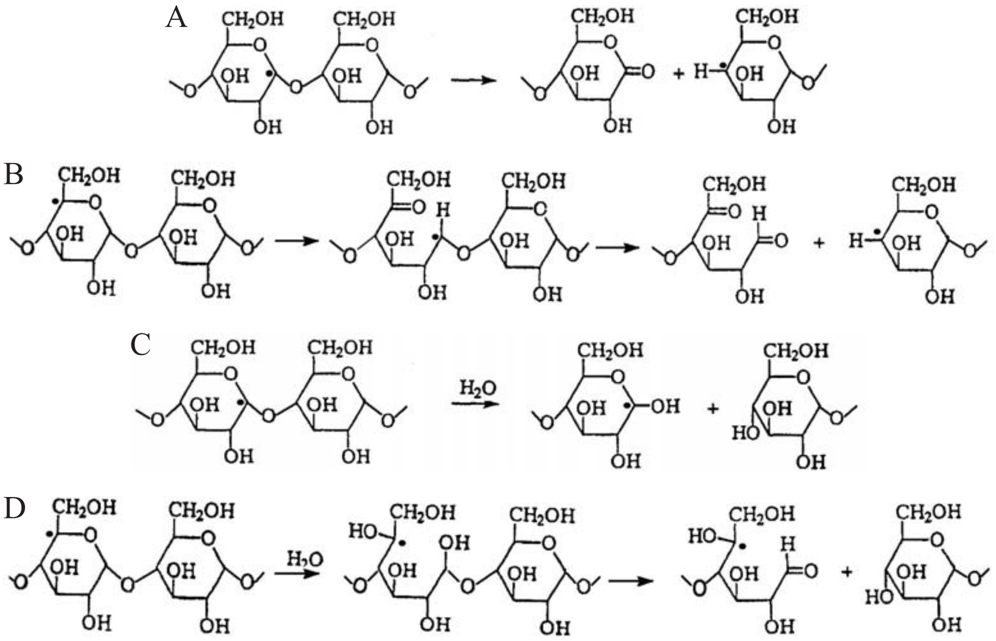
Fig.3. The structure of κ-carrageenan, ι-carrageenan, and λ-carrageenan.

Some oligosaccharides, such as chitosan, carboxymethyl chitosan (CM-chitosan), carrageenans or alginates, containing functional groups, as amide, sulfate or acid, show biological activity, as antibacterial, antiviral and antiphytoviral, antitumor, hemostatic, immunomodulation, *etc*., as well as antioxidant activity. Such activity may not be observed or is less efficient in the case of the same polysaccharide having a high molecular mass. Biological activity can be correlated to the oligosaccharide type, a specific range of the molecular mass, and the degree of substitution and conformation (which effects accessibility to active sites) [2-8]. Thus, chitosan shows antimicrobial activity, but this activity is higher in the case of oligosaccharides with a lower molecular mass [2-4] and might mainly be related to the presence of the amide groups. Macromolecular carrageenan does not show biological activity, while such activity, depending additionally on the sulfonation level, was found for some carrageenan oligomers. Carrageenans are a good example of the dependence of biological activity on the oligomer conformation, as in Fig.3; κ-carrageenan shows the highest biological activity.

3. BASIC RADIATION PROCESSES INVOLVING POLYSACCHARIDES

The differences in structure of particular polysaccharides affect their radiation processing and efficiency. Such differences in radiation processing can also happen for various conformations of the same polysaccharide (*i.e.* various forms of carrageenans). In the case of heteroglycans (*i.e.* alginates), the radiation processes depend on the participation of a particular monomer unit on the polysaccharide chain.

The formation of primary free radicals and their interaction with solvent are found with polysaccharides which follow the same rules as do free radical reactions with synthetic polymers. Free radicals are formed mainly by disruption of C–H linkages [8-10]. Secondary free radicals are formed on carbon atoms. For example, chain reactions of the primary and of the secondary free radicals lead to a disruption of the glicosidic linkages or C–O and C–C linkages in the glucose residues [9-11]. The transformations of free radicals formed on C1, C4 and C5 lead to fragmentation resulting in the formation of saccharides and carbonyl derivatives [9]. Examples of reactions taking place in the dry solid state and in an aqueous environment are presented in Scheme 2. Rearrangements of the oxide and superoxide radicals formed in the presence of oxygen result in the formation of carboxylic acids.



Scheme 2. Example free radical reactions taking place in the dry solid state (A, B) and in an aqueous environment (C, D).

Use of radiation processing for polysaccharides modification

Degradation resulting from the cleavage of glycosidic linkages is the most probable effect of ionizing radiation on solid polysaccharides and on polysaccharides in solution. Water soluble ether and ester polysaccharide derivatives (shown in Fig.2) degrade as do non-substituted polysaccharides when irradiated in the solid state or in aqueous solutions at low concentration (below *ca.*

10 wt%). An increase in the concentration above some critical value, which is well determined for each individual polysaccharide, leads to competitive crosslinking. In the systems characterized by a high polysaccharide concentration, in the so-called paste-like state, crosslinking occurs instead of degradation. Further increases in polysaccharide concentration result again in the predominance of degradation over crosslinking. Because of the decrease in mobility of the polymer chains with increases in concentration, the crosslinking reaction becomes restricted and at high polysaccharide concentrations, there is a predominance of degradation over crosslinking.

Besides crosslinking and degradation, polysaccharides can be grafted with monomers by using radiation processing.

4. DEGRADATION OF POLYSACCHARIDES

Radiation-induced degradation of alginates, carageenans, chitosan, pectin, cellulose, and starches are well recognized processes used mainly for making oligomers with well determined molecular mass. This relates to the potential uses of oligosaccharides in agriculture, as food hydrocolloids, in pharmacy, and in the plastics industry. An important reason for degrading or scissioning oligosaccharides is to modify their biological and antioxidant activity.

This degradation is accompanied by the formation of carbonyl and carboxyl products (compare Section 3).

4.1. DEGRADATION PROCESSES FOR POLYSACCHARIDES

A decrease in the mean molecular mass of a polymer (M_w/M_n) results from degradation, as shown in Fig.4. This is indicated by a decreased capability to form a gel and by a decrease in the viscosity of any gels that are formed.

Doses up to 500 kGy and sometimes even up to 1000 kGy have been used for polysaccharide degradation in dependence on polysaccharide type and the desired modifications. However, doses greater than 100 kGy were rarely used. To obtain the same level of depolymerization it was necessary to irradiate solid polysaccharides with an absorbed dose that was around thirtyfold higher as compared to irradiation carried out in a dilute aqua solution. This occurs due to the fact that irradiation in the solid state involves direct irradiation effects; whereas irradiation in water initiates indirect effects from water radiolysis products, their propagation and their subsequent reactions with the polymer. The extent of depolymerization was greater after irradiation of solutions done in air as compared to irradiation conducted under nitrogen. This is

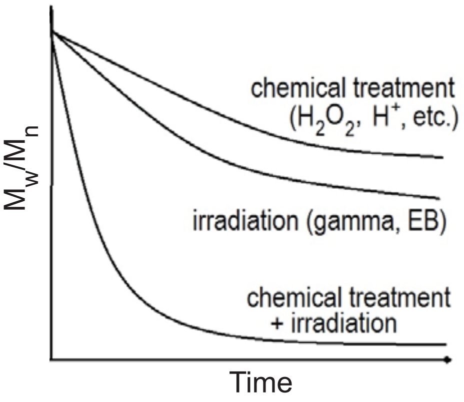


Fig.4. Schematic presentation of the degradation process of polysaccharides under: chemical treatment, gamma irradiation (at a defined dose rate), and the action of gamma irradiation on the solution of chemical agent.

related to the differences between the radiation processes and the products formed during irradiation. The irradiation of dilute solutions/gels done under nitrogen formed products containing C=C linkages; while irradiation under oxygen leads to the formation of C=O groups [11]. These differences were not noticed in the degree of depolymerization when the irradiation was carried out for solid samples either in air or in nitrogen, using the same irradiation doses, with there being smaller effects of irradiation performed on solid samples as compared to those irradiated in solution.

Differences were found between the sensitivity to irradiation for various forms of the same polysaccharides depending on their structure. For example, the following sequence was found to be the case for particular carrageenans structures, shown in Fig.3, based on both the formation of C=C linkages and the desulfonation level obtained after irradiation [8]: λ-carrageenan > ι-carrageenan > κ-carrageenan.

Synergistic effects of irradiation and chemical/enzymatic treatment

The combination of ionizing radiation with chemical treatments (acid or oxidative degradation) produces oligomers with a required molecular mass by using lower irradiation doses and has more efficient control of the structure and properties of the products as compared to using each of these processes separately [6, 12-14]. Examples are the irradiation of chitosan in diluted acetic acid solutions [13] or of the oxidative degradation of chitosan and alginate carried out in H_2O_2 solutions [6, 14] or of other systems that generate $^{\bullet}OH$ radicals. Figure 4 illustrates the effectiveness of combining processes. For example, it was found [14] that a dose of 4 kGy was sufficient for effective degradation when carried out in the 1% H_2O_2 solution, with no effect on the degree of deacetylation. M_w decreased to around 60% of the non-irradiated chitosan after treatment for 24 h with 1% H_2O_2, and up to around 10% after gamma irradiation in water solution using a 32 kGy dose. Irradiation of a 1%

H_2O_2 solution produced a similar degree of depolymerization after using a dose of 4 kGy.

Another example is the effective radiation-initiated degradation of solid chitosan which had been previously subjected to oxidative degradation carried out in solutions containing H_2O_2, $NaNO_2$ or NaClO.

Low molecular weight, active polysaccharides were made using irradiation of H_2O_2 solutions of chitosan, CM-chitosan, and alginate. These oligomers showed strong antioxidant properties, dependent on the molecular mass, and, in the case of the alginate, on the participation of two structural units (guluronic acid and mannuronic acid) in the polysaccharide chain [6]. Irradiation of alginates in 2% H_2O_2 solution produced a several-fold higher superoxide anion scavenging activity as compared to when irradiation was carried out in the absence of H_2O_2.

Conditions that limit undesirable degradation

Degradation is not desirable, for example, in the area of conservation of paper and wood artifacts which require some decontamination.

To protect systems containing polysaccharides against degradation that takes place under radiation decontamination various conditions were modified. Besides conducting the processes at low temperature, in the absence of oxygen, or after the addition of antioxidants, the irradiation of polysaccharides dispersed in protecting solvents that can act as free radicals scavengers was carried out. Some ionic liquids, *i.e.* 1-butyl-3-methylimidazolium chloride (Bmim), acted as radical scavengers [15]. Irradiation of wood moisten with Bmim improved the water resistance of the wood surface and limited water penetration [16].

Potential use of radiation-initiated degradation in industry and in environmental protection

The studies were carried out tending to support some industrial processes by ionizing radiation. Radiation pretreatment of lignocellulosic or cellulosic biomass or cellulose pulp, before enzymatic, acid or alkali hydrolysis, facilitated the degradation of the materials [17-19] and could be used as a step in the processes leading to the isolation of cellulose from biomass [17], in the production of alkali cellulose or bioethanol [18] as well as in utilization of waste products [19]. The simultaneous action of radiation treatment and acid hydrolysis (3% H_2SO_4) was also examined. The doses used varied in the range from 25 up to 1000 kGy. The radiation treatment alone is not effective enough for the degradation of lignocellulosic materials regarding the strong effect of lignin presence.

4.2. MODIFICATION OF THE ACTIVITY OF OLIGOSACCHARIDES

The activity of polysaccharides depends both on the molecular mass and on the presence of the specific functional groups. The radiation degradation process should be conducted at the conditions that enable to produce oligomers with the desired molecular mass and to preserve active functional groups.

For example, κ-carrageenan has the highest activity among the carrageenans. Irradiation induces smaller changes in it as compared to the other carrageenan conformations, as noted above (desulfonation) [8]. Using the appropriate irradiation conditions, κ-carrageenan can be made with a slightly decreased sulfonation level but with a high enough degree of depolymerization so that a long-lasting active agent may be produced. Thus, κ-carrageenan appeared to be the most promising polysaccharide for making the active carrageenan oligomer using irradiation [8].

Defense against phytoviruses

Phytoalexins are the defense substances synthetized by plants to protect them against phytoviral diseases. When used to feed plants, solutions of small amounts of oligosaccharides favor the formation of such compounds. Such oligosaccharides can be made by using radiation processing. Irradiation at a dose of 1000 kGy produces pectin and chitosan oligomers which have similar activity as enzymatically prepared products. The irradiation of chitosan produces particularly large amounts of phytoalexin, specifically pisatin [20, 21].

Increasing the antimicrobial, antifungal and antioxidant activity

Using of chitosan oligomers prevents the growth of bacteria, fungi and molds. Chitosan oligomers made using irradiation processing can extend the time of microbial incubation as compared to the non-irradiated chitosan.

For example, as reported in Ref. [16], *Escherichia coli* bacteria were detected immediately after incubation in a culture grown without chitosan. With non-irradiated chitosan, having an initial molecular mass equal to around 700 kDa, incubation time was about 7 h. With chitosan that was irradiated in the solid state to a dose of 50 kGy incubation time reached about 15 h, and no bacteria appeared when chitosan was irradiated to a dose of 100 kGy. However, use of a dose of 500 kGy and higher leads to decreases in the antimicrobial activity. The incubation times were as follows: 500 kGy – about 60 h, 1000 kGy – about 30 h, 1500 kGy – about 20 h, and 2500 kGy – *ca.* 3 h [4]. The most active fractions of chitosan have M_w in the range of 100-300 kDa.

For example, the use of irradiated chitosan was more efficient in protecting fruit against spoilage. When fruits were coated with non-irradiated and with irradiated chitosan, the irradiated chitosan extended shelf-life from 7 to 15 days [4].

Antioxidant activity was detected for the oligomers of chitosan, alginate and carrageenan made using irradiation processing [6, 7].

Promoting plant growth

Watering plants with the extracts of polysaccharide oligomers (carrageenans, alginate, chitosan, lignocellulose) made using gamma irradiation lead to an enhancement of plant growth [8, 20-22]. For example, when alginate having M_w equal to about 7000 kDa and made using irradiation (in the solid state with a dose of 500 kGy or in a 4% solution with 100 kGy) was introduced into the hydroponic cultivation of rice, there was a 15-40% increase in biomass yield with dependence on the irradiation conditions and on the concentration of the alginate solution [20, 21].

The differences in the structure and susceptibility to irradiation of particular carrageenans resulted in differences between their biological activities and the changes of this activity resulting from irradiation. Native κ-carrageenan has shown the highest activity compared to the other carrageenans [20]. A comparison of the action of carrageenans irradiated to doses of 100, 500 and 1000 kGy has shown that the highest biomass yield was obtained after using of κ-carrageenan irradiated to a dose of 100 kGy (Table 1).

Table 1. The approximate biomass yields estimated basing on Ref. [20] for the cultivation fed with κ- and ι-carrageenans.

Dose [kGy]	κ-carrageenan [%]	ι-carrageenan [%]
0	40	8
100	85	35
500	40	45
1000	40	5

Further studies [2] have shown that the best effect on the growth of potatoes was observed after using carrageenan irradiated to a dose of 30 kGy. The biological activity of κ-carrageenans in plants is related to their M_n in the following order: 1 kDa < 3 kDa < 5 kDa.

The following conclusions can be drawn about carrageenans action on plant growth (based on data from Refs. [20] and [8]):

- Native: κ-carrageenan > ι-carrageenan.
- Sensitivity to irradiation: κ-carrageenan > ι-carrageenan.

There is an optimum dose which can be used to obtain the highest effect on promoting plant growth for particular carrageenans. In the case of κ-carrageenan, irradiated in the solid state, the following sequence indicates that dose greater than 30 kGy is less effective [2]: 30 kGy > 100 kGy > 500 kGy (1000 kGy – inhibited, ineffective).

Suppression of environmental stress in plants

The contamination of soil with salt or heavy ions negatively effects plant growth. The presence of lignocellulosic materials extracted from biomass or of some other oligosaccharides diminishes this effect. The activity of such materials is increased by irradiation. For example, soil contaminated with salt reduces the biomass yield by 63%. The addition of non-irradiated and irradiated lignocellulosic extracts (from palm oil fiber) to the contaminated soil increased the yield to 93 and 103%, respectively [21].

5. CROSSLINKING OF POLYSACCHARIDES AND GRAFTING POLYSACCHARIDES

Although natural polysaccharides easily form gels in water, crosslinking produces hydrogels suitable for practical applications. Gels can also be made with hydrophobic derivatives of polysaccharides. In such cases, the other solvent must be trapped in the polysaccharide matrix.

Hydrogels for biomedical and industrial applications are commonly prepared by crosslinking water soluble synthetic polymers, such as poly(vinyl alcohol) (PVA), polyvinylpyrrolidone (PVP), poly(ethylene oxide) (PEO), poly(acrylic acid), polyacrylamide, and polyacrylonitrile. There is increased interest in "bio-artificial" polymers made from synthetic and natural polymers, often a polysaccharide or a polysaccharide derivative. Hydrogels based exclusively on natural polymers, polysaccharides or compositions of polysaccharides and proteins, are also of interest. Multicomponent hydrogels can show improved capability for swelling, modification of the sensitivity to pH, ionic strength or temperature as compared to hydrogels based on a single respective component. A low stability in water, however, is an important limitation for the use of polysaccharide hydrogels, despite of their beneficial properties.

As with hydrogels based on synthetic polymers, hydrogels based on polysaccharides can serve as the matrices for the immobilization (microencapsulation) of the "guest" molecules or particles. This process consists of immobilizing solid particles, microdrops of liquids or bioparticles (proteins, peptides, antibodies, cells or enzymes), in a matrix of a crosslinked polymer by physical bonding and/or physical entrapment in the gel network. This can be done by polymerization or crosslinking of polymer together with the entrapped component. Microencapsulation prolongs the action of the active components because of slower and controlled release, depending on environmental conditions, such as pH. The resulting hybrid materials can be used as the major components of artificial organs as well as in various controlled delivery systems. This deals with drug delivery as used in medicine and pharmacy, biocatalyzers, catalyzers used in the chemical industry, fertilizers used in agriculture, *etc*. The immobilization of microdrops of liquids permits the substitution of liquid oils by solid powders, which simplifies some processes in food industry.

Hydrogels based on polysaccharides can be made by crosslinking the polysaccharide alone, crosslinking a system containing a polysaccharide and a synthetic polymer, or by grafting the polysaccharide. The crosslinking of polysaccharides can be performed using a chemical method with the use of a crosslinking agent, such as glutaral aldehyde or genipin. Radiation processing is also widely used for the crosslinking and grafting of polymers. To obtain products with good properties, the processes must be carried out in such a way that the crosslinks will occur between two adjacent polymer chains and not within the same chain. In the case of grafting, the formation of the large amount of the grafted copolymer with a low amount of homopolymer is preferred. In the past two decades methods for the radiation crosslinking of polysaccharides have been developed which can be used in a variety of delivery systems. In the case of biomedical applications, it is beneficial to select the conditions for crosslinking a hydrogel such that the irradiation dose used for crosslinking relates to the sterilization dose of 25 kGy.

Materials crosslinked by irradiation have already found or are expected to find biomedical uses, in particular as wound dressings (including bioactive dressings), in drug delivery systems, as dietary supplements, for cushioning bedsores, as well as for use in the cosmetics industry. Many of these materials show appropriate properties to find use as absorbents and soil stabilizers. The ability of various crosslinked hydrogel materials to absorb metal ions and dyes has been confirmed.

Crosslinking of polysaccharide derivatives

Crosslinking can be effectively done using ether or ester derivatives of polysaccharides in a paste-like state. Crosslinking occurs through the mobile side chains (Fig.2).

First hydrogels made using the radiation processing of carboxymethylcellulose (CMC) were described by Fei *et al.* and Wach *et al.* in 2000 [23, 24]. The authors assumed that in the case of CMC, radiation crosslinking was more effective compared to crosslinking done by chemical methods. Radiation processing was used to make hydrogels based on systems that did not include any synthetic polymer; whereas the chemical crosslinking of highly substituted CMC could only produce a slight amount of crosslinked polymer [24].

Radiation processing experiments conducted with various ether and ester derivatives of polysaccharides produced hydrogels based on CMC, CM-chitosan, carboxymethyl chitin (CM-chitin), carboxymethyl starch (CMS), methyl cellulose (MC), hydroxyethylcellulose (HEC), hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose phthalate (HPMCP), *etc*. [25-30]. Some crosslinking of the non-substituted chitosan and starch was observed [31-32].

Several factors influence the radiation process and consequently the properties of the resulting products: polysaccharide type, degree of substitution (DS), concentration of the solution being irradiated, solvent type, absorbed dose and atmosphere during irradiation.

The evidence of crosslinking is shown by formation of gel, as illustrated in Fig.5. As crosslinking progresses, the gel content increases with an increase in the hardness of the gel and a decrease in swelling capability, as in Fig.5. The minimum dose needed to initiate gel formation is called the gelation dose. Doses that ensure appropriate high efficacy of the crosslinking processes might be considerably higher. It should be remembered that degradation and crosslinking are two competing processes taking place in all irradiated materials during the radiation process.

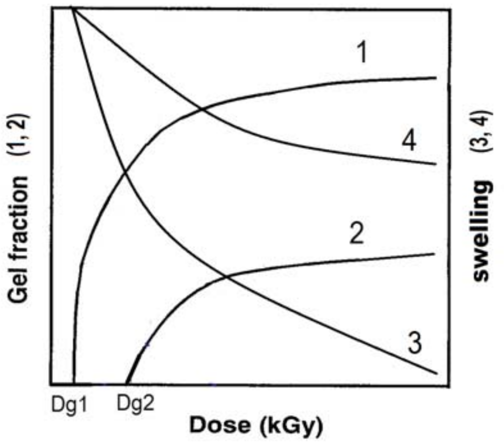


Fig.5. Schematic presentation of the dose dependence of gel formation and swelling for crosslinked polysaccharide systems: high efficiency – curves 1 and 3, low efficiency – curves 2 and 4. Dg1 and Dg2 mean the appropriate gelation doses for each type of process.

In general, a high degree of the polysaccharide substitution and a high concentration of the liquid medium favor making highly crosslinked materials, as in Fig.5. Fei *et al.* [23] observed that in the case of CMC, the efficiency of crosslinking increased when the degree of substitution increased to 2.2 and was the highest at concentrations of 20 to 30%. The effect of concentration is related to the fact that, at high concentrations, the nearest polymer chains can be close enough to each other to overcome any repulsive forces. However, with further increases in concentration, the mobility of the chains becomes too low and the probability of interaction between two adjacent chains decreases. Accordingly, the gelation dose depends on the concentration of the solution and reaches a minimum value (optimum) at a well-defined concentration. As a consequence, the optimum concentration for carrying out the most effective crosslinking should be determined separately for each particular crosslinked system.

As can be expected, the higher efficiency of crosslinking might be attained when the process is carried out in vacuum or under nitrogen, as compared to the process being carried out in the presence of oxygen (air) [23, 24].

The gelation doses for water soluble derivatives of cellulose, chitin and chitosan are relatively low, around 3 kGy. The doses needed to achieve effective crosslinking are, however, in the range of 20 to 40 kGy. Increasing dose above some critical values causes degradation of the crosslinked material.

In the case of CMS, effective crosslinking was found at lower doses compared to the carboxymethyl derivatives of other polysaccharides [27]. The effective dose determined for CMS, with a degree of substitution of 0.15, was 5 kGy in cases when irradiation was carried out in 15-50% water dispersions, and the highest efficiency of crosslink formation was observed after irradiation for dispersions with a concentration of 40%. In those instances in which there was an intermediate concentration, the content of the crosslinked material decreased when the dose was increased to above 10 kGy. The crosslinked CMS also forms hydrogels with high swelling capability, *i.e.* 1000 g/g after irradiation at a dose of 2 kGy. The lower costs resulting from the effectiveness at lower doses together with the lower price of CMS make it possible to produce hydrogels and adsorbents at lower costs compared to those based on other polysaccharides.

A majority of the crosslinking experiments were carried out in water and aimed at the preparation of hydrogels. However, crosslinking of the hydrophobic polymers is also possible when the polymer is dissolved in organic solvent or in a water solution of a salt, such as Na_2CO_3 [28, 29]. The type of solvent strongly affects the properties of the resulting gels. This effect is related to the formation of different free radicals which originate from each individual solvent due to irradiation, and to the further reactions of these radicals with polymers. For example, the formation of crosslinks in HPMCP takes place with the higher efficacy in methanol as compared to methyl acetate or to acetone [28]. The high mobility of polymer chains in a solvent also favors the formation of more crosslinks, as the polymer chains get closer one to another. Accordingly with solvents of the same type, the mobility of the polymer decreases when its chain length increases. This results in lower crosslinked density after irradiation. The gelation doses found for HPMCP were in the range of 50-60 kGy and the doses that are highly effective for crosslinking are even as high as 300 kGy [28]. This is considerably higher as compared to the water-soluble polysaccharides.

Hydrogels made by the above methods show good properties as adsorbents which are sensitive to the pH of the solution. In the cases of CMC, CM-chitosan and CM-chitin, the highest swelling ratio was achieved after using low doses, only 3 kGy. However, making hydrogels with an appropriately high mechanical resistance for use as the material in beds requires using higher doses [24, 25]. 1 g of CMC gels crosslinked in a 15% solution using doses of 3 and 40 kGy are capable of absorbing 500 or 300 g of water, respectively [30]. However, the higher crosslinked product made using a dose of 40 kGy is preferred. CMC hydrogels, crosslinked using a dose of 50 kGy, have similar mechanical resistance as hydrogels based on the synthetic polymers, and high enough swelling properties. This, together with the relatively low cost of CMC, creates opportunities for the wider use of those hydrogels as absorbents in industry and in agriculture. Functional groups in crosslinked chitosan and chitin are capable of selective binding of cations while having high swelling capability. These materials have thus the appropriate properties for use as absorbents for metal ions [26].

Crosslinked cellulose derivatives are used in pharmaceutical applications for drug encapsulation. Although the activity of the crosslinked material is lower than the base material, hydrogels made using radiation crosslinked CM-chitosan still show high antimicrobial potential and it makes them of interest in active wound dressings.

Crosslinked systems made with PVA, PVP, PEO

The introduction of the natural polysaccharides such as agar, carrageenans, chitosan or starch [33-40] into hydrogels based on PVA, PVP or PEO compositions before subjecting them to radiation crosslinking increases mechanical resistance, increases the water/solvent gain and, in some instances, imparts biological activity. In particular, the hydrogels of carrageenan with PVP or PEO absorb especially high amounts of water (over 13 000 g/g) [35] and show high mechanical strength allowing them to be used as absorbents in industry. The polysaccharide to synthetic polymer weight ratios varied from 1:10 to 3:1. Crosslinking was done in solutions containing 55 to 20% of the total polymer mass.

The structure of the mixed hydrogels is, in general, described in terms of the physical blend constructed from two interpenetrating polymer networks (IPN). However, two networks might entangle each other and interact *via* hydrogen bonding and electrostatic or ionic forces. The polysaccharide chains probably form a stiff skeleton while more flexible chains of the synthetic polymer can be entangled or entrapped within the gel matrix of polysaccharide.

The formation of crosslinks in radiation processing probably takes place with the participation of the synthetic polymer. Degradation is the major process taking place in the polysaccharide component. However, partial crosslinking or grafting of the polysaccharide and synthetic components can also take place. This concerns hydrogels of PVA or PVP with agar, carrageenan [33-35] and starch [39] (despite of the fact that majority of the starch is incorporated as a bulking agent in the PVA/PVP networks). Crosslinks form after the use of low doses in the range up to 10 kGy [34]. The other reports show that the structure resulting after irradiation of PVA (PVP)-agar and PVA (PVP, PEO)-carrageenan systems may constitute two tangled gel networks, whereas CM-chitosan is immobilized in the crosslinked PVA/PVP matrix [38].

The above studies were carried out using PVA(PVP)-polysaccharide solutions containing 5-10% of the synthetic polymer and irradiated at doses up to 100 kGy. The appropriate selection of the irradiation doses is especially important for the mixed hydrogels because of the concurrence process of polysaccharide degradation. The dose of 10 kGy was an optimum for making hydrogels containing carrageenan [36]. For example, for this polysaccharide and at this dose, the highest level of the crosslinked products, the highest strength and a high water absorption were attained. In the case of PVP/CM-chitosan, the use of higher doses of radiation might be more profitable [37], as in the cases of the systems containing only polysaccharides.

The introduction of chitosan or CM-chitosan into hydrogels based on PVA, PVP or PVA/PVP gives them an antimicrobial activity [36, 37] and results in an increase in the capability to bind to proteins, whereas hydrogels containing carrageenan show hemostatic activity [35]. These properties might be profitable for use in active dressings (*i.e.* antimicrobial, hemostatic) or in delivery systems for protein-based drugs.

Present development of hydrogels based on mixed systems is aimed at the preparation of multicomponent materials containing together several polysaccharides and synthetic polymers and the systems showing biological activity (antimicrobial, hemostatic). Such materials are foreseen for use as modern multifunctional adsorbents or in a biomedicine.

Grafting of monomers onto polysaccharide matrices

Radiation processing has been also used for grafting water soluble monomers onto starch and chitosan matrices [41-42] for use in products as absorbents. Acrylate monomers and their various derivatives were used as the graft monomers. The doses needed to attain a high degree of grafting (up to 70% of the monomer) were in the range of 2-8 kGy. Optimal properties were obtained at a monomer to starch ratio of 2:1 or 2.5:1.

The other purpose for grafting water soluble as well as water insoluble monomers (*i.e.* styrene [43]) onto starch matrices is to produce degradable materials that can be added to polyolefins in order to make partially biodegradable plastics having better mechanical properties compared to those manufactured with addition of just starch that was not grafted.

6. PREPARATION AND MODIFICATION OF BIODEGRADABLE AND EDIBLE PLASTICS

The environmental problem of increasing amounts of non-degradable plastic waste has generated interest in substituting some of these plastics, particularly those used traditional packaging materials as films and foams with novel materials based on natural and biodegradable polymers. Such materials could possibly be used as edible packaging (films and coatings) in the food and pharmaceutical industries. Such biodegradable materials should also have appropriate mechanical, barrier and sometimes sensory properties.

Polysaccharides have good film forming ability and make strong films when prepared by solution casting. However, some serious disadvantages of such materials are their high affinity to water and the dependence of mechanical properties on water content, which results in high strength films with low flexibility or low strength films with somewhat higher flexibility. Various strategies have been used to optimize polysaccharide film properties. Modification methods have been used for the polysaccharide substrates, such as degradation, crosslinking, esterification, etherification, and oxidation. Other solutions have dealt with compositions made from several polysaccharides or based on polysaccharide-protein systems. The blending of polysaccharides with biodegradable synthetic polymers, introducing hydrophobic additives (waxes, lipids, surfactants, *etc*.) or the use of reinforcing agents such as inorganic particles or fibers have also been looked at. Appropriate physical or chemical treatments are used to improve the cohesion of the polymer chains in blends. Bulk as well as surface modifications have been used for this.

Increasing interest in the use of safe and longer lasting packaged foods has generated interest in active packaging materials which would have antimicrobial or antioxidant activity [44]. This can be achieved by the introduction of active polysaccharide or other active additives (*i.e.* essential oils) into the material.

The use of the nano-sized particles or fibers results in plastics with the improved properties compared to the materials prepared with addition of the micro-sized additives. Nanocomposite systems can have also advantages when used for the delivery of active components.

Radiation modification was successfully used at the various steps in preparing films with improved functional properties or biodegradability. Radiation-initiated modification of the materials was done before the films were made. Radiation processes were also used to improve the compatibility of the film's components, to modifiy surface properties, as well as grafting the film material while in solution or on the surfaces of films. The irradiation of these packaging films has a high practical impact. This is related to the radiation decontamination of packaging materials and to the use of sterile packaging materials.

In majority of cases the doses used for systems containing polysaccharides were in the range up to 30 kGy, with higher doses being the exception. The best results were found after using doses in the range of 10 to 20 kGy.

Irradiation of solid polysaccharide before making films

The irradiation of a polysaccharide is profitable for some starch or a starch-surfactant compositions [45]. This is because good quality films or coatings could be more easily made when viscosity of the film forming solution was relatively low but with a high concentration of solids. Oxidized starches, which simultaneously degrade, are used. When radiation degradation is accompanied by oxidation, the irradiation can substitute for chemical methods. For example, the gamma irradiation of the potato starch substrate with absorbed doses in the range 5 to 30 kGy with an optimum of 10 to 20 kGy showed an improvement in the mechanical properties of films along with a decrease in hydrophilicity. The addition of a surfactant, sodium monolaurate, at an appropriate level in the composition along with using the irradiated starch produced films with hydrophobic properties. The contact angles for films made using non-irradiated starch and starch irradiated to 30 kGy were 58.4 and 100.4°, respectively. In addition to the starch being oxidized, the improvement in films properties resulted from the increased homogeneity of the films, as confirmed by scanning electron microscopy (SEM) [46].

Irradiation carried out using film forming solutions

Irradiation conducted for solutions containing polysaccharide or a composition based on polysaccharide-synthetic polymer-protein systems, with dry solids content being about 3 to 10 wt%, also produced better films. For example, improvements in the mechanical and barrier properties of the pectin-PVA (1:1), pectin-gelatin-PVA film, or the starch-locust bean gum-PVA films [47, 48] were observed after irradiation with gamma rays at doses up to 30 kGy. In the case of pectin-gelatin-PVA films (1:1:0.5) a dose of 10 kGy, when combined with crosslinking in a $CaCl_2$ solution, leads to 1.3-fold increase in tensile strength and a decrease in water vapor permeation of 0.8 of the initial value. However, in the case of alginates [49], the improvement of mechanical properties accompanied by decrease in swelling capability was found only after using a low dose of irradiation (optimum at 0.5 kGy), while additional dose leads to the films with the again inferior properties.

The improvement in the functional properties of these films can be explained by the crosslinking of the components that takes place in solutions.

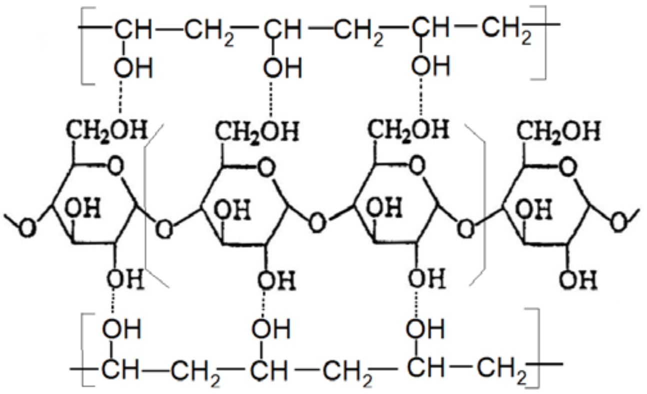
Irradiation carried out in the paste-like state

Pastes consisting of 25% of starch or up to 50% a total dry mass of polymer (starch, starch-chitosan and starch-bean protein) were irradiated then compression molded [32, 40, 50-52]. Irradiation up to 50 kGy increased the strength and elasticity of the films with a decrease in their hydrophilicity [32, 50, 51]. Using higher doses caused a decrease in the strength of starch and starch-chitosan films [32, 50]. Starch-chitosan films had increased antimicrobial and antifungal activity, compared to films based on non-irradiated compositions, demonstrating an occurrence of degradation processes (compare Section 4). The introduction of PVA leads to a deterioration the film properties [52], regarding the PVA crosslinking and initiating hydrogel formation [40] (compare Section 5). In such cases, good quality foams were produced [40].

Irradiated pastes containing about 50% dry solids have been successfully used for the compositions based on flours made from some leguminous plants [51].

Irradiation of films

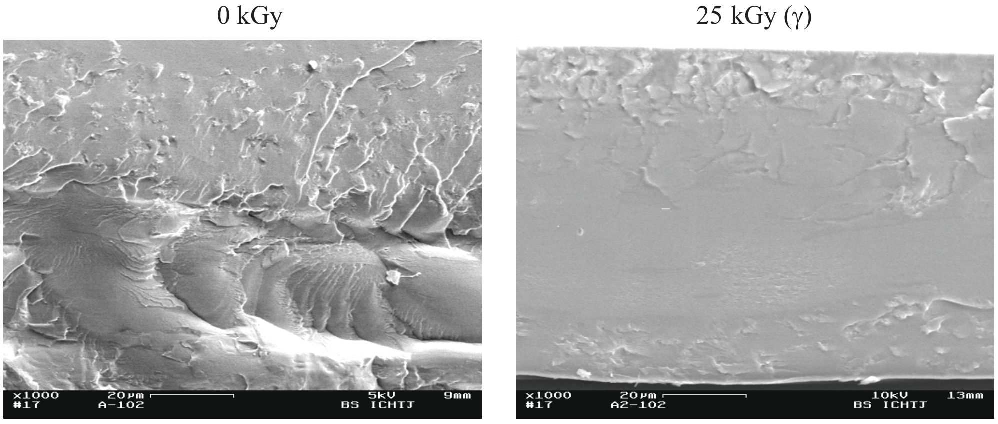
Although degradation of polysaccharide is expected with the use of pure polysaccharide, surface as well as bulk crosslinking also takes place when multicomponent systems based on several polysaccharides or on polysaccharide-protein-synthetic polymer systems are used [53, 54]. The proposed mechanism of hydrogen bonding in a starch-PVA system is shown in Scheme 3. This results in increased tensile strength in films and a decrease in elasticity. Although the radiation process took place in bulk, surface modification is especially important.



Scheme 3. The proposed mechanism of hydrogen bonding in a starch-PVA system.

Irradiation with gamma rays and with fast electrons in air causes oxidation, especially surface oxidation, as confirmed by the formation of C=O groups in films based on pure polysaccharides, as starches and chitosans, as well as starch-PVA films [55, 56]. This leads to increased hydrophobic properties of films, as shown by a considerable increase in contact angle to water (*i.e.* going from 69 to 88° [55]).

The improvement of the functional properties of multicomponent films after irradiation is due to their increased homogeneity besides chemical processes. Examples are starch-lignin films irradiated with fast electrons to 200 and 400 kGy [57] or starch-PVA films irradiated with gamma rays to 25 kGy, as shown in Fig.6 [55].



0 kGy

25 kGy (γ)

Fig.6. SEM images of the fracture of starch-PVA films (50:50, 30% of glycerol), non-irradiated and irradiated [55].

The use of gamma and/or electron beam irradiation was found to be an effective way to improve the properties of films based on starch-PVA, MC, MC-chitosan, starch-chitosan and CMC-sodium alginate compositions [53-55, 58-60], including those containing cellulose nanocrystallites (NCC). Irradiation improved the properties of films that contained natural antioxidants, such as gallic acid, ferulic acid or tyrosol. This effect was attributed to formation of crosslinks between the polymer chains *via* flexible molecules of the antioxidants [61].

Currently an important question arises concerning the effects of irradiation on the properties of bioactive films and coatings made by physical entrapment of guest molecules in the polymer network as their activity and possible release of the active component into a packaged product.

Radiation grafting of hydrophobic and active agents

Radiation processing can be used to improve the mechanical and barrier properties of the polysaccharide films by radiation grafting of appropriate monomers. 2-Hydroxyethyl methacrylate (HEMA) monomer was added to polysaccharide solutions before casting of films as based on MC, chitosan, starch or chitosan-starch compositions [62, 63]. Irradiation of the films with relatively low doses, from 1 up to 25 kGy, depending on the composition, improved the film strength, elasticity, and moisture barrier properties.

Radiation techniques can be also used to graft active components on films. This can be done by activation of the polymeric matrix using radiation treatment followed by immersion in the solution of the active component [64].

Introduction of NCC modified by radiation supported grafting a natural antioxidant (gallic acid) into gellan gum films improved the functional properties of the films, as compared to those containing none or the unmodified NCC [65].

Protection of food by edible coatings and irradiation

Protecting foodstuffs with coatings based on radiation-modified polysaccharides might help prolong their shelf-life as compared to the coatings based on non-modified materials. Food protection was more effective when active components were introduced into the film compositions, in particular when an active polysaccharide (*i.e.* chitosan) was used as the substantial component. In this case, the protective effect was strengthen after irradiation (compare Section 4).

The protection of foodstuffs by covering them with edible coatings was combined with the preservation of the food using irradiation. Two procedures have been proposed: (i) the first procedure is to irradiate the food and then cover it with the coatings, and (ii) the second is to irradiate the food after coating it with a protective layer [66]. The advantage of the second procedure is that it can modify the properties of the final coating using irradiation and to produce sanitized product and modified packaging within the same process. However, only relatively low doses, up to 2-3 kGy, are permitted for some food preservation. Thus, the possibility of using radiation modification of the coating during food irradiation is rather limited.

7. RADIATION MODIFICATION OF COMPOSITES AND POTENTIAL IN OTHER AREAS

Nanotechnology and advanced materials using polysaccharides

Irradiation is beneficial in making and functionalizing biopolymer plastics containing nanoparticles, such as metal or oxide particles, carbon nanotubes, nanopolysaccharides, *etc*. This includes the use of radiation to immobilize nanopolysaccharides in biopolymer matrices for tissue engineering. Modification of these materials is conducted in relation to the modification of properties as potential scaffolds.

Radiation methods can be used for making and functionalizing polysaccharide nanoparticles. Radiation method might thus substitute or support two "conventional" methods for making polysaccharide nanoparticles or nanofibers which rely on the mechanical destruction of the fiber or on the selective acid hydrolysis of the amorphous regions in the grain or fibers. Irradiation changes the polysaccharide similar to changes made by acid or mechanical treatments. The process consists of irradiation of a water dispersion of a polysaccharide followed by the precipitation of particles [67, 68]. It was possible to diminish the mean size of starch particles from 450 to 174 nm after irradiation with an absorbed dose of 300 kGy [68].

The surface of polysaccharide nanoparticles can be functionalized to impart hydrophobic or hydrophilic properties and to modify the activity of nanoparticles by grafting with appropriate functional groups [65].

The use of ionizing radiation for the restoration of cultural heritage objects

The deterioration of paper during storage is a consequence of cellulose degradation. This is an intrinsic process of oxidative degradation taking place under influence of atmosphere and of oxidative substances present in the paper or of acid hydrolysis due to the presence of acids. Biodeterioration and the destruction of wood and paper may also be due to the action of molds, fungi and insects.

Besides disinfection, consolidation techniques are used to improve the physical properties of wood and paper artefacts [69]. Consolidation consists of introducing monomers into the recovered object and internally polymerizing them using ionizing radiation. These processes were developed in several research centers in Europe (in France, Romania, and Germany) and are used for particular cultural artifacts. The technology paper consolidation was established at the Fraunhover Institute for Electron Beam and Plasma Technology in Germany.

Food industry (food additives, foodstuffs, feedstuffs)

The ability to form gels indicates a wide use of polysaccharides and their modifications in the food industry as additives for shaping and preserving food structure. Radiation-induced degradation [70] as well as crosslinking [71] can be used for the modification of the functional properties of food hydrocolloids and the functional properties of food containing polysaccharides as well as to facilitate polysaccharides extraction from grains. Rheological properties of food, emulsification and foaming properties, water and oil adsorption are dependent on food hydrocolloids. The degradation processes of starch, cellulose and proteins that take place when irradiating foodstuffs and feedstuffs were examined to see how they facilitated digestibility of the products [72]. The doses used during the studies were in the range of 3 kGy.

8. SUMMARY AND CONCLUSIONS

The large variety of possible structural types of polysaccharides provides a diversity of physical properties and potential reactivity. The most important physical property of polysaccharides is their high affinity for water. This property determines numerous uses in the food industry, in the biomedical area, in industry and in environmental protection. At the same time, this restricts the use of plastics based on polysaccharides. Depending on the required properties of the each particular product, it is necessary to optimize the polysaccharide system of choice.

Ionizing radiation initiates numerous processes in biopolymers. The differences in the structure of a particular polysaccharide or even its conformation as well as specific arrangements of structural units in the chain affect the radiation process, its course and efficiency. The basic reactions taking place in polysaccharides are still not fully understood, but it is possible to control the process result for a respective polysaccharide by modification of the irradiation conditions. In the case of non-substituted polysaccharides, the major process, taking place in the solid state and in an aqueous environment, leads to scissioning of the glycosidic linkages, although a variety of additional reactions take place. Oxidation processes play an important role. The irradiation of ether or ester derivatives of polysaccharides in the paste-like state leads to crosslinking. The relation between degree of degradation and crosslinking depends on the degree of substitution of the polysaccharide and on its concentration in solutions or pastes. Irradiation grafting of some monomers leads to materials characterized by some unique properties.

Trials are now being carried out to develop new fields for the use of ionizing radiation with systems containing polysaccharides. Using ionizing radiation generates new products which can find novel applications, improves the properties of the known products or can remove biological contaminants from new objects. In particular, irradiated polymers are used for making hydrogels suitable for medicinal use, for absorbents in industry or in agriculture. Oligosaccharides made by radiation processing, in particular active oligosaccharides, are foreseen for uses in medicine, agriculture and the food industries. Irradiation is used for the modification of biodegradable and edible plastics, especially for packaging films and coatings. This includes active packaging being looked at for a variety of delivery systems, especially those which can be used in the food and pharmaceutical industries, but which are also being explored for use in agriculture and chemistry. The grafting of the active components can be done using irradiation. Biodegradable plastics might also find use as coatings in tissue engineering and as coatings or adhesives in the paper or textile industries. Irradiation might be also used in the development of nanomaterials (nanoparticles and nanocomposites), based on polysaccharide systems, as well as for modification of food and food additives or for the consolidation of cultural artifacts.

Radiation-initiated degradation of polysaccharides or lignocellulosic materials can also be used in conjunction with degradation processes carried out by using chemical agents or enzymes. In some industrial processes, for example in the paper or textile industries, radiation can improve the methods of extraction the polysaccharides from raw sources and the use of industrial or agricultural wastes.

Besides new technologies based on polysaccharides, irradiation can be used for the decontamination of food and food additives as well as for the recovery of cultural heritage artifacts and for the sterilization of hybrid materials containing polysaccharides. Methods have been developed to protect those materials against undesired changes caused by irradiation. Accordingly the study of the radiation effects on polysaccharide-based materials is of importance.

The irradiation of polysaccharide containing systems has already found or has potential to find use in plastics technology, in nanotechnology, in medicinal and pharmaceutical areas, in the food industry, in the chemical and other technical industries, in the conservation field, in agriculture and in environmental protection. The ease and relatively low costs of regeneration, recycling or use of products based on natural polymers developed from renewable resources. as compared to petrochemical synthetic polymers, can have a positive impact on the environment and on the global economy.

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