- O_2: retention time – $t_R(O_2) = 2.77$ min, coefficient of hydrogen – $R(O_2-H_2) = 2.5$, coefficient of nitrogen – $R(O_2-N_2) = 3.7$, coefficient of peak symmetry – $A_s(O_2) = 1.2$, number of theoretical shelves – $N(O_2) \approx 488$.
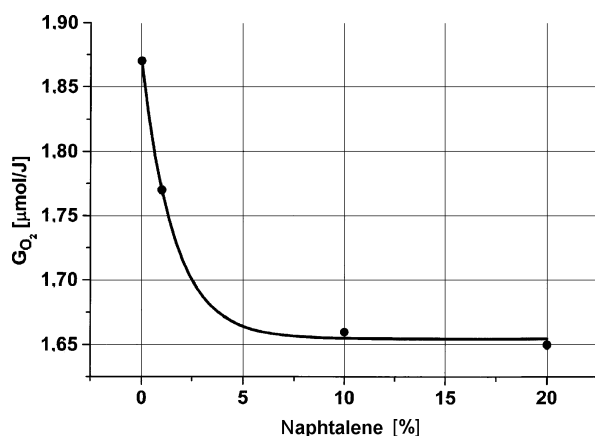

Fig.3. Relation between naphtalene concentration in polypropylene and radiation yield of oxygen.

The described method has proved its efficiency in the description of protective action of naphthalene towards degradation of polypropylene [4] (Fig.3). That method helped also to show that the rate of radiation-induced oxidation of polypropylene at low temperature (under liquid nitrogen) is higher than at ambient temperature (Fig.4). That is the first exception of the rule of rather lowered radiation yields of radiation-induced reactions at cryogenic temperatures. Further investigations in
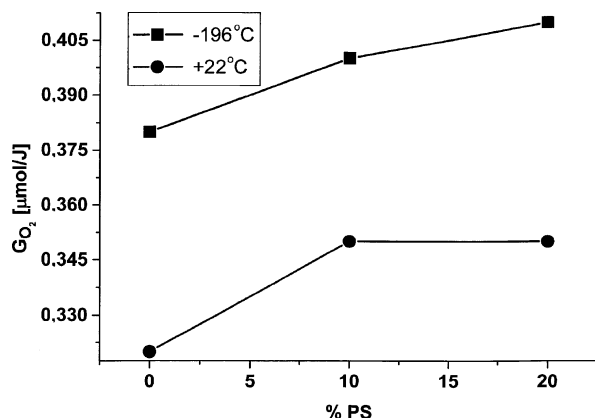

Fig.4. Relation between polystyrene concentration in polypropylene/polystyrene blends and radiation yield of oxygen in temperature: ■ -196°C, ● +22°C.

this fragment of radiation chemistry will show to what extent physical conditions in the system are responsible for that exceptional behaviour.
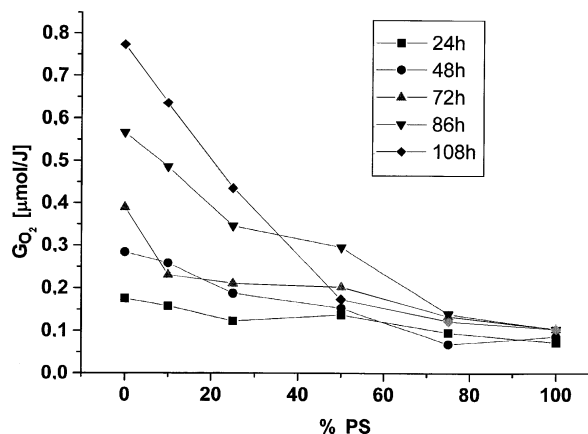

Fig.5. Relation between polystyrene concentration in polypropylene/polystyrene blends and radiation yield of postirradiation oxidation processes (postirradiation time: 24-108 h).

The gas chromatographic method has been applied also in the study of postirradiation oxidation processes of ageing polymers (Fig.5). The loss of oxygen helped to trace the oxidation process, and the parallel production of hydrogen has helped to estimate the participation of aromatic compounds in the process of blocking peroxide groups and crosslinking with the polypropylene chain. These processes interrupt the cycle of polymer degradation and can help in branching of chains, thus improving properties of the material. Analysis of the influence of polystyrene (PS) content on the oxidation process shows that the protection effect is higher in the case of samples undergoing a longer ageing process. One can explain that by the improved contact of aromatics with the polypropylene matrix.

These few examples have shown that a simple and sensitive at the same time analytical method helps to investigate not only radiation oxidation phenomena but also photo- and thermooxidation.

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CHEMICAL-RADIATION DEGRADATION OF NATURAL POLYSACCHARIDES (CHITOSAN)

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Naturally occurring polysaccharides have a wide range of applications in agriculture, medicine and cosmetics, food industry and water waste treatment.

Chitin is second, next to cellulose, most abundant polysaccharide on the earth. It is present in crustacean shells, insect exoskeletons and fungal cell walls.

Chitosan, (1-4)-2-amino-2-deoxy-β-D-glucan, is deacetylated derivative of chitin. Commercially available chitosan possesses high molecular weight and low solubility in most solvents what limits its applications. The solubility of chitosan can be improved by decreasing its molecular weight [1]. Water soluble chitosan can be prepared through oxidative degradation with hydrogen peroxide in concentration higher than 1 M [2]. Low molecular weight chitosan can be prepared by chemical, radiation or enzymatic degradation of a high molecular weight polymer. Radiation is one of the most popular tools for modification of polysaccharides. For decreasing of the polymerization degree, combined chemical-radiation methods can also be used. Chitosan oligomers were obtained through irradiation of chitosan dissolved in acetic acid [3]. Another popular method is also chemical degradation with hydrogen peroxide which even in small quantity reduces gradually molecular weight of chitosan [2]. Treating plants with oligochitosan increase their disease resistance and also plant growth is stimulated. Degraded polysaccharides such as alginate, chitosan or carrageenan can increase tea, carrot or cabbage productivity by 15 to 40% [4]. Chitosan irradiated with 70-150 kGy strongly affect the growth of wheat and rice plant and reduces damages caused by vanadium. [5]. Alginate degraded with radiation at concentration 20-50 ppm promotes the growth of rice seedlings, at a concentration of 100 ppm it causes an increase of peanut shoots by about 60% compared to control [6]. Foliar application of chitosan on pepper plants reduces their transpiration and water use and the biomass-to-water ratio is significantly better in the treated plants compared to the control plants [7]. Chitosan can also be used in plant protection from diseases because it is a strong antimicrobial agent [8].

The goal of this work was to use radiation for polysaccharide structure modification. Depolymerization of chitosan can be carried out by radiation or oxidative degradation with hydrogen peroxide
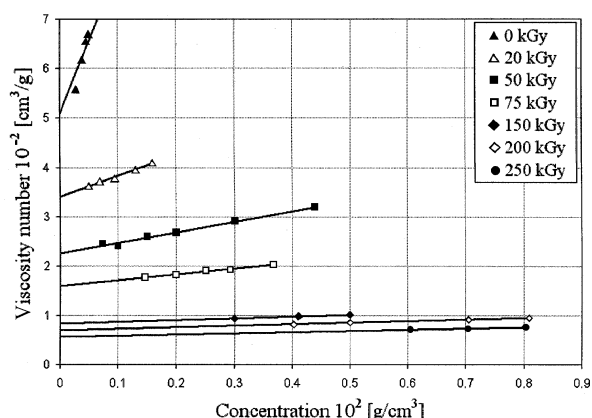

Fig.1. Results of vicometric measurement of chitosan modified with ionizing radiation.

combined with irradiation with electron beam. Efficiency of degradation methods was verified by viscometric measurements using an Ubbelohde capillary viscometer k=0.01073. Average molecular weights were calculated from the equation:
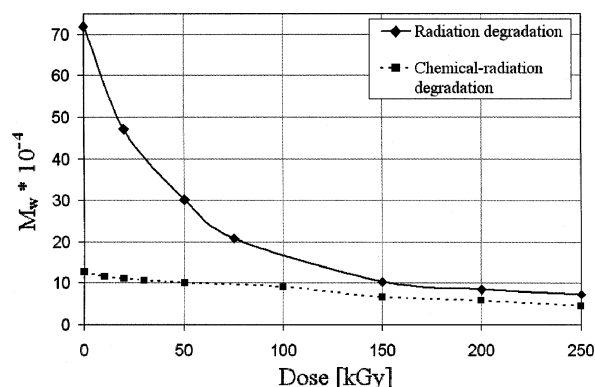

Fig.2. Radiation and chemical-radiation degradation of chitosan.

$$[\eta] = K \cdot M_w^a$$

where: $[\eta]$ – intrinsic viscosity; M_w – average molecular weight; K and a – constants for chitosan independent of molecular weights, $K=1,81 \cdot 10^{-3}$ cm^3/g and a=0.93 determined in 0.1 M acetic acid and 0.2 M sodium chloride solution at a temperature of 25°C [9]. Results of vicometric measurement of chitosan modified with ionizing radiation are shown in Fig.1.

Results shown in Fig.2 indicate that irradiation of a dry powder of chitosan lead to the reduction of molecular weight. The M_w decreased remarkably with increasing dose up to 200 kGy. For higher doses, there was no significant change in molecular weight. Hydrogen peroxide caused breaking of 1,4-β-D-glucoside bonds, used at small concentration caused a rapid decrease of molecular weight. Increasing concentration or reaction time did not affect the further decrease of polymerization degree. Chitosan degraded with the chemical-radiation method attained 95% mass reduction. Using hydrogen peroxide at the first stage of degradation the required doses of radiation can be decreased what is much more appropriate from the economical point of view.

Figure 3 shows the X-ray diffraction patterns of initial chitosan and modified chitosan. Initial chitosan and after radiation exhibited two characteristic peaks at 2θ=8.9° and 2θ=20.2°. There is no change in intensity of the peaks. Radiation degradation did not destroy crystal structure of chitosan.
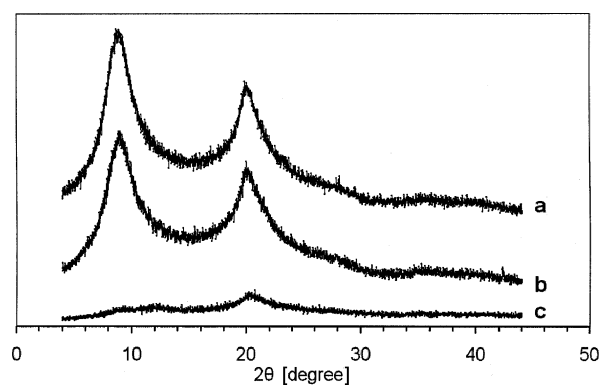

Fig.3. X-ray diffraction patterns of (a) initial chitosan, (b) chitosan after radiation degradation with a dose of 250 kGy and (c) chitosan after chemical-radiation degradation.

For chitosan after chemical-radiation degradation, the first peak is not observed and the peak at $2\theta = 20.2°$ is much less intensive. The results show that chemical-radiation degradation of chitosan caused destruction of the crystal structure.

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DSC STUDIES OF GAMMA IRRADIATION EFFECT ON INTERACTION OF POTATO STARCH WITH THE SELECTED FATTY ACIDS AND THEIR SODIUM SALTS

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Differential scanning calorimetry (DSC) appeared to be the appropriate method for detection of gamma irradiation influence on starch interaction with lipids [1-3]. Structural modification of macromolecules and possible changes in the lipid surrounding induced by gamma irradiation, as well as possible modification of the lipid molecules, were found to affect the properties of the inclusion amylose-lipid complexes formed with naturally occurring lipids on heating wheat starch and flour (A-type) [1,2]. Our preliminary DSC studies have also shown differences between the complexes formed by irradiated and the non-irradiated potato starch (B-type) and admixed 1-mono-lauroyl glycerol [3].

Currently, the effect of potato starch irradiation with ^{60}Co gamma rays using a 30 kGy dose was studied on its interactions with two fatty acids (lauric and palmitic) and their sodium salts.

Irradiations with ^{60}Co gamma radiation were carried out in a gamma cell "Issledovatel" in the Department of Radiation Chemistry and Technology, Institute of Nuclear Chemistry and Technology. DSC studies were carried out using a DSC calorimeter of TA Instruments instaled in Vrije Universiteit Brussel (Belgium). DSC studies were carried out during several heating-cooling-heating cycles with a heating and cooling rate of $10°Cmin^{-1}$. The Universal Thermal Analysis Package was applied for data analysis. The suspensions placed in hermetically closed pans were characterized by the surfactant : polysaccharide : water ratio of 1:10:10. This corresponds to 0.498 mmol of lauric acid, 0.390 mmol of palmitic acid, 0.458 mmol of sodium laurate and 0.359 mmol of sodium palmitate per 1 g of starch. DSC studies were carried out during several heating-cooling-heating cycles with a heating and cooling rate of $10°Cmin^{-1}$. Additionally, some complementary studies were continued with a heating and cooling rate of $5°Cmin^{-1}$ applying the smaller lipid to starch ratios. These values correspond to 0.274 and 0.137 mmol of sodium laurate

or sodium palmitate per 1 g of starch and 0.274 and 0.68 mmol of palmitic acid per 1 g of starch.

Melting of dry solid lauric and palmitic acids are accompanied by endothermal effects with peaks at 45.2 and 65.5°C. Melting of both sodium salts occurs at a considerably higher temperature and is accompanied by double thermal effects with peaks at *ca*. 122 and 135°C. No influence of water presence was noticed on the temperature range of melting of both fatty acids, while melting of both sodium salts occur under such conditions at a considerably lower temperature. During the first heating, melting of lauric acid and sodium laurate in water takes place in a temperature range lower
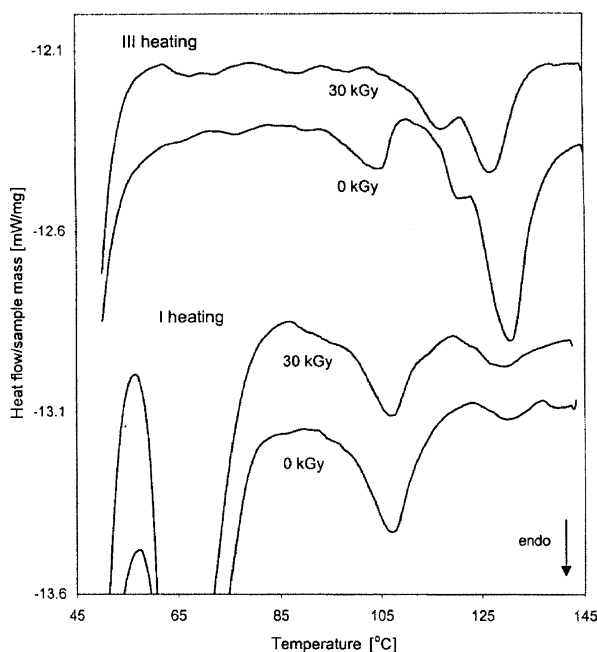

Fig.1. Thermal effects attributted to the melting of amylose-lipid complexes recorded during the first and third heating of the system containing lauric acid admixed to the non-irradiated and irradiated starch (at weight ratio equal to 1:10).