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Controllable degradation of polysaccharides stimulated by electron-beam plasma

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The natural renewable biopolymers chitin and, its deacytelaited derivative chitosan are very promising for technological and industrial applications such as agriculture, medicine and pharmaceutics, food processing, cosmetics production and others [1]. In medicine and pharmaceutics the water-soluble low molecular weight oligosaccharides (less than 10 kDa) are usually required. To produce the low molecular weight chitooligosaccharides several techniques, including chemical, enzymatic, and radical treatment have been suggested [2]. Nevertheless the development of the effective techniques for quick and environment friendly chitin and chitosan degradation is the burning issue of the day.

The novel approach to the water-soluble low molecular weight chitooligosaccharides production based on the Electron Beam Plasma (EBP) application is considered in the present paper. The EBP is generated by injecting an electron beam (EB) into a gaseous medium. Under typical conditions of the EBP generation (medium pressure 1-100 Torr and moderate EB power (less than 1 kW)) the plasma is strongly non-equilibrium and cold. The generated EBP has a complex composition and contains a lot of chemically active particles that do not exist under equilibrium conditions.

Crab shell chitin and chitosans were treated in EBP using the specially designed Electron Beam Plasmachemical Reactor (EBPR) [3]. Fig. 1 illustrates the design and operation of the EBPR used for the biomaterials modification. The focused EB 3 generated by the electron-beam gun 1 which is located in the high vacuum chamber 2 is injected into the working chamber 5 filled with the plasma-generating gas through the injection window 4. In passing through the gas the EB is scattered in elastic collisions and the energy of fast electrons gradually diminishes during various inelastic interactions with the medium (ionization, excitation, dissociation). As a result, the EBP cloud 10 is generated, all plasma parameters being functions of x, y, and z coordinates (z is the axis of the EB injection).

The electromagnetic scanning system 12 placed inside the working chamber near the injection window is able to deflect the injected EB axis in x and y directions and, therefore, to control the spatial distribution of the plasma particles over the plasma bulk. The working chamber is preliminary evacuated to pressure 10^{-5} Torr and then filled with the plasma generating media. The experimental conditions were as follows:

- the plasma generating gas oxygen at the pressure 5 Torr;
- the distance between the injection window and sample surface – 250 mm;
- the EB scanning mode – concentric circles with maximal diameter 130 mm;
- treatment time was varied from 1 to 20 min;
- to prevent thermal destruction all samples were processed at material temperature less than 70 °C.

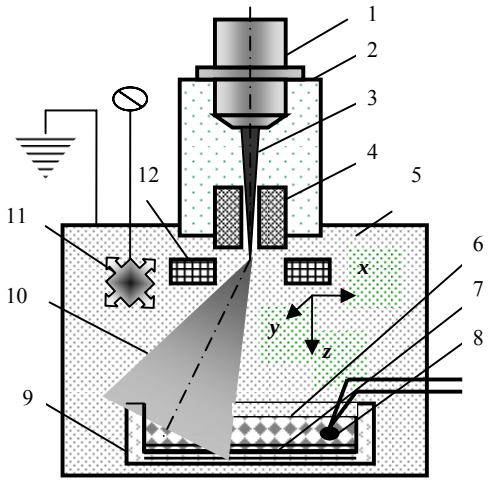

Fig. 1. The design of the plasmachemical reactor and the treatment procedure of polysaccharides powders. 1 – electron beam; 2 – high vacuum chamber; 3 – EB; 4 - injection window; 5 – working chamber; 6 – mixing layer of the powder to be treated; 7 – piezoceramic plate; 8 – temperature sensor; 9 – glass container; 10 – EBP cloud; 11 – water evaporator; 12 – scanning system.

Low molecular water-soluble forms of chitosane were obtained by its treatment in the EBP of oxygen. The exclusion chromatography of the EBP-treated chitosans revealed the formation of a number of LMWC with molecular weight 800 - 2000 Da and polydispersion 1,5 – 5,0. The degradation of the original polymer is due to the effect of free radicals formed in the EBP. Active oxygen particles (oxygen radicals, atomic and singlet oxygen) that are produced in plasmachemical processes seem to be the most important.

The 95% yield of low molecular weight EBP-treatment products was attained by optimizing the treatment procedure. The high yields of low molecular weight water soluble products are obtained at treatment time ~ 10 min whereas the traditional chitosan hydrolysis usually takes several days. The hazardous by-products and toxic wastes are not generated during the EBP-treatment.

The low molecular water-soluble forms of the chitosan obtained by its treatment in the EBP of oxygen and water vapor were found to inhibit the growth of yeast-like and filamentous fungi.

Thus, our experiments showed that the EBP can be used for the effective and controllable degradation of natural biopolymers chitin and chitosan and that the active radicals produced in plasmachemical processes are responsible for the modification. The technique involved is likely to be promising to engineer the low molecular weight compounds with unique pharmacological and biological activities and the EBPRs seem to be competitive with the traditional chemical chitin and chitosan hydrolysis.

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