Electron Beam Plasma processing of chitosan powders and solutions: possible approaches

T. Vasilieva[1], M. Vasiliev[2], Zaw Ye Myint[2], Khin Maung Htay[2], and Htet Wai Yan Kyaw[2]

[1]*Department of Chemistry, Moscow Institute of Physics and Technology, Dolgoprudny, Russia*
[2]*Aerospace Research Department, Moscow Institute of Physics and Technology, Dolgoprudny, Russia*

Abstract: Approaches to the controllable processing of chitosan powders and solutions by means of low temperature Electron Beam Plasma and Hybrid Plasma are described. Water-soluble chitooligosaccharides with weight-average molecular mass M_w ~ 600 Da and polydispersity 1.5 were formed due to the plasma chemical treatment of original chitosan. Advantages of the plasma chemical technologies based on electron-beam plasmas over conventional methods of chitosan are also considered.

Keywords: electron beam plasma, hybrid plasma, chitosan, plasma-stimulated processing, green technologies.

1. Introduction

Natural renewable biopolymer chitosan (deacytelaited derivative of chitin) is very promising for technological and industrial applications such as agriculture, pulp and paper subsector, microbiology, food processing, and especially in medicine, pharmacology and pharmaceutics [1, 2]. For practical applications water-soluble low molecular weight (bellow 10 kDa) chitooligosaccharides (COS) are usually required. For example, in agriculture COS are used as elicitors, stimulators of plant growth and antimicrobial agents against a wide spectrum of phytopathogens [3].

To produce COS several techniques, including chemical, enzymatic, and radical treatment by γ-irradiation and high-energy electron beams (with energies MeVs) have been suggested [4]. Simple and rather low-cost chemical treatment is a conventional method, however toxic wastes and environment contamination are inherent in chemical chitin and chitosan processing as well as in all techniques mentioned above. Besides, the chemical treatment is very time consuming and usually takes several hours. The radiation treatment is also complicated because of limited controllability of treatment conditions, high power consumption, and operation complexity of electron accelerators and γ-radiation isotope sources. Thus, the development of the effective techniques for quick and environment friendly chitosan degradation is the burning issue of the day.

The plasma chemical technologies based on non-equilibrium low temperature plasmas could be considered as a promising alternative to the methods mentioned above. The approaches to the processing of chitosan powders and solutions with Electron Beam Plasma (EBP) are described in the present paper.

2. Processing of Chitosan Powders in Electron Beam Plasma

The EBP is generated by injecting an electron beam (EB) into a gaseous medium. Under typical conditions of the EBP generation (medium pressure $1 < P_m < 100$ Torr and moderate EB power $N_b < 1$ kW) plasma is strongly non-equilibrium and cold.

For the EBP-processing of chitosan powders Electron Beam Plasmachemical Reactor (EBPR) was designed [5].

Fig. 1 illustrates the design and operation of the EBPR. The focused EB 3 generated by electron-beam gun 1 that is located in high vacuum chamber 2 is injected into working chamber 5 filled with the plasma-generating gas through injection window 4. In passing through the gas the EB is scattered in elastic collisions and the energy of fast electrons gradually diminishes in 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).

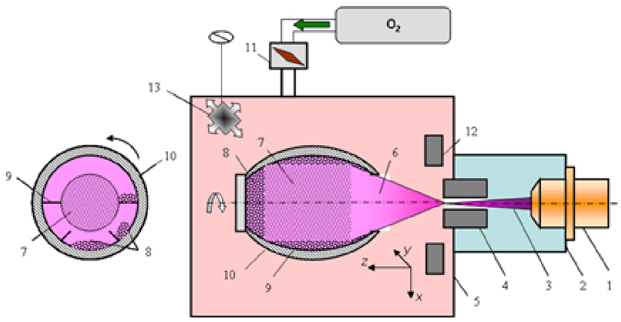

Fig. 1. The EBPR design and chitosan powder treatment procedure.

1 – electron beam gun; 2 – high vacuum chamber; 3 – EB; 4 – injection window; 5 – working chamber; 6 – EBP cloud; 7 – aerosol reaction zone; 8 – polysaccharide powder to be treated; 9 – internal partitions; 10 – cylindrical quartz vessel; 11 – gas feeder; 12 – scanning system; 13 – water evaporator.

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 a 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.

To produce COS in amounts sufficient for practical uses (up to tens or even a hundred of grams) the EBPR was equipped with a rotating mixer. The device was placed inside the EBPR working chamber filled with the plasma generating gas at required pressure. The powder was loaded into the mixer and the EBP was generated inside the mixer volume; as a result, aerosol reaction zone 7 is formed inside the chamber (Fig. 2).

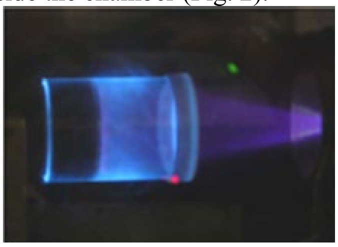

Fig. 2. The EBP generation and chitosan powder treatment inside rotating mixer.

The optimized conditions were as follows [6]:

- plasma generating medium was water vapor at P_m = 5 Torr. Bidistilled water vapor was produced by water evaporator 13 (Fig. 1) placed inside the EBPR working chamber;
- distance between the injection window and sample surface – 250 mm;
- the EB scanning mode – concentric circles with maximal diameter 130 mm;
- treatment time τ was 10 min;
- to prevent thermal destruction of chitosan all samples were processed at material temperature T_s = 40 °C. The sample temperature was monitored during the treatment by non-contact IR-pyrometer Optris LS (Optris GmbH, Germany). The temperature was controlled by selecting the EB current I_b ($1 < I_b < 100$ mA).

High molecular weight crab shell chitosan (viscosity-average molecular weight M_v = 500 kDa) with the degree of deacetylation 85% and polydispersion 1.5, was used as an original substance for the further EBP-treatment.

3. Characterization of the COS structures resulted from the plasma-stimulated processing.

The chitosan crystallinity index (CI) was determined by the XRD technique. Preliminary experiments revealed CI loss in the following ranges: from 61.1-65.9% for the original chitosan up to 50.9-55.2% after the EBP-treatment.

The exclusion chromatography of the chitosan treated in the water vapour EBP revealed the formation of COS with weight-average molecular mass M_w ~ 600 Da and polydispersity 1.5.

The analysis of the IR absorption spectra (Fig. 3) of the original and treated chitosan showed that the EBP-treatment resulted in some increase of oxygen-containing carbonyl C=O and carboxyl –COOH groups (the bands at 1735 cm^{-1} and 1650 cm^{-1}) and some destruction of the β-1,4-glycosidic bonds (decrease in the integral intensity of the bands at 1155 cm^{-1} and 896 cm^{-1}).

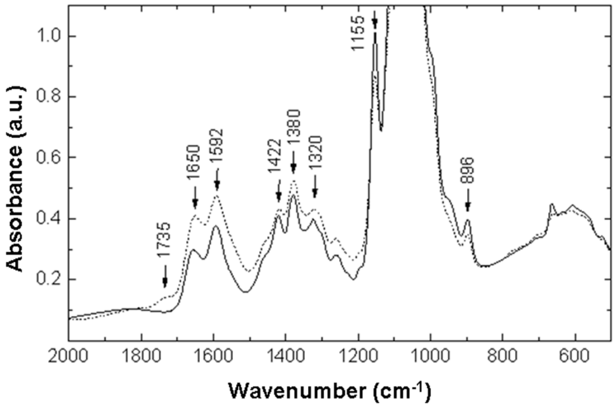

Fig. 3. Chitosan absorbance spectra fragments before (solid curve) and after (dashed curve) the EBP-processing in the range 500-2000 cm^{-1}.

Table 1. The advantages of the EBP-stimulated chitosan processing with respect to conventional methods.

Criteria	Hydrolysis method		
	Chemical hydrolysis	Radiation methods	EBP-stimulated processing
Treatment duration	Several hours or days	Usually several hours	Minutes (τ ~10 min)
Efficiency	Biopolymer amorphous parts destruction predominates. Low yields of COS and large amounts of monomeric units	Molecular mass decreases but 2-3 times. High polydispersion of products	COS from dimeres to heptatamers are produced. Destruction of both amorphous and crystalline parts of biopolymer occurs. COS yield up to 80-85%
Number of stages	Multi-stage	Multi-stage: additional treatment in alkaline solutions are needed	Single-stage
Ecological safety	High concentrated acidic or alkaline solutions are needed. Toxic wastes are produced. High energy consumption	High concentrated acidic or alkaline solutions are needed	Environmentally friendly: hazardous by-products and toxic wastes are not generated

The deacetylation degree of the EBP-treated chitosan was measured by ^{1}H NMR. The analysis revealed the deacetylation degree was slightly increased after the EBP-processing from 85% (original chitosan) to ~97%.

4. The comparison of the EBP-stimulated chitosan destruction with respect to conventional methods

The advantages of the EBP-stimulated chitosan processing with respect to conventional methods are summarized in Table 1.

In contrast to traditionally used hydrolysis techniques the EBP-stimulated hydrolysis is rapid single-stage, and environment friendly procedure.

The advantages of the EBP-treatment with respect to gas discharge plasmas have been discussed in our previous papers [6, 7]. In addition, the effective controllable destruction of polysaccharides occurs due to the EBP-hydrolysis whereas the treatment in gas discharge plasmas mostly results in biomaterial oxidation and its hydrophilic properties improvement [8].

5. Other approaches to the chitosan processing: chitosan solutions processing in the EBP

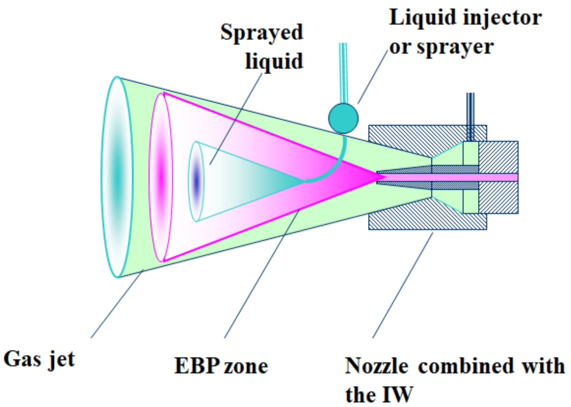

Fig. 4. Generation of the EBP containing sprayed liquids.

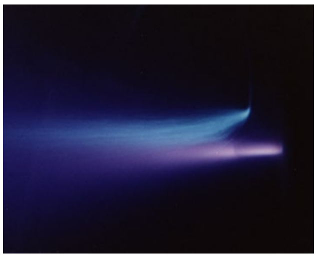

Fig. 5. The injection of chitosan solution into the EBP flow.

One of the main EBP peculiarities is the possibility to generate stable high-speed gas flows in which liquid droplets can be sprayed [7]. Thus chitosan solutions can be modified in the EBP. Solutions of high molecular weight chitosan in 1% acetic acid and solutions of low-molecular COS formed by means of the EBP-processing chitosan powder were used to implement this approach (Fig. 4 and 5).

The EB can be combined with another ionizer, e.g. with a gas discharge. In the latter case the so-called Hybrid Plasma (HP) is generated [7] where very high (super-equilibrium) concentrations of chemically active particles are obtained even at low (down to room) temperatures. The HP-stimulated chitosan degradation was also proved experimentally; the time of COS formation was reduced by 20% with respect to the EBP-processing.

6. Conclusions

The results of our study demonstrate that the EBP-technology is promising for effective, resources saving, and environmentally friendly processing of chitosan powders and solutions.

The water-soluble COS produced in the EBP and products of the EBP-modification of chitosan solutions can be used as:

- Active components for novel hybrid bioactive materials with combined properties (e.g., hemostatic/antibacterial).
- Biodegradable scaffolds for Regenerative Medicine with enhanced cell adhesion and growth.
- Active components for addressed drug delivery systems and systems for controllable drug release.
- Active components for plant biostimulators and fertilizers.
- Components for biosensors.
- Materials for effective sorbents, filters, and membranes (e.g., for wastewater treatment, hemodialysis, etc.).
- Materials for food conservation and active packaging.

In general, plasma chemical technologies based on electron-beam plasmas may be considered as an alternative to conventional methods of natural polymers (chitin, cellulose, lignins and many others) processing.

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8. References

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