# DEGRADATION RATE OF SOME ELECTRON BEAM IRRADIATED STARCHES

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*Lucrarea prezintă rezultate experimentale privind influența tratamentului cu fascicul de electroni asupra distribuției maselor moleculare şi a vitezei de degradare pentru amidonurile de porumb şi cartof. Datele obținute au arătat că tratamentul cu fascicul de electroni conduce la formarea unor fragmente cu diferite mase moleculare, care modifică distribuția de masă a amidonurilor, în funcție de doza de iradiere. Viteza de degradare a fracțiunilor de masă depinde de proveniența botanică a amidonurilor.*

*The paper presents the experimental results regarding the influence of the electron beam treatment on molecular weight distribution and degradation rate of corn and potato starch. The obtained data showed that the electron beam treatment lead to the formation of fragments with different molecular weights, which modify the molecular weight distribution of investigated starches as a function of the irradiation dose. The degradation rate of molecular weight fractions dependeds on botanical source of starches.*

**Keywords:** molecular weight distribution, degradation index, corn, potato

## 1. Introduction

Starch is one of the natural materials which get attention lately as a consequence of the global interest regarding renewable, cheap and easy to process resources. It is composed of two major constituents based on α-D-glucose, amylopectin – the branched component – and amylose – the linear component [1] conferring unique properties global macromolecule.

In many applications, specific molecular weight of polysaccharides is required [2]. Electron beam (e-beam) irradiation is known as a method able to degrade polymers both in solid and liquid state. Radiation processing of polysaccharides is based on the generation of free radicals that are capable of

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inducing molecular changes by decomposition of macromolecules and the creation of molecules with smaller chains [3].

Recent studies [4-6] have showed that the e-beam treatment may change some physicochemical properties of different starches as a consequence of the molecular weight degradation.

Degradation rate evaluation of starch macromolecule subjected to e-beam irradiation can help in different applications when certain molecular weight is desired. Thus, the aim of this paper is to evaluate the radiodegradation rate of corn and potato starches based on their molecular weight distribution determined by GPC analysis.

## 2. Experimental

Corn and potato starches used in the experiments have been purchased from the Romanian commercial system. The packed starch samples were irradiated with e-beam up to 50 kGy using a linear accelerator with medium energy of 6MeV (INFLPR, Bucharest-Magurele, Romania), at ambient temperature and normal pressure. The irradiation doses were measured using cellulose triacetate film.

The samples for GPC analysis were prepared according to the method described by Han and Lim [7] slightly modified. Thus, starch (10 mg) was wetted with ethanol (20 µl), and then dispersed in 1M NaOH (500 µl). The mixture is then magnetically stirred (1000 rpm) for 10 minutes at $35^0$ C. The starch solution obtained was diluted to 50mM NaOH with water, and gently stirred again (150 rpm) for 30 minutes at room temperature, followed by centrifugation (3500 x *g*, 10 min). GPC analysis was performed using a Breeze system (Waters, USA) which consists in 1525 binary pump, autosampler 717+, 2414 differential refractive index detector, in-line degasser AF and temperature modul system. The calibration was carried out with pullulan standards for two Ultrahydragel columns (Waters, USA). The mobile phase used for GPC was 50mM NaOH and the flow rate was 0.5 ml/min. The obtained data were analyzed with Breeze v. 3.30 SPA software.

## 3. Results and discussion

Number average molecular weight ($M_n$), weight average molecular weight ($M_w$), z-average molecular weight ($M_z$) were determined for studied samples in order to reveal the influence of the e-beam treatment on molecular weights and distribution. Table 1 shows the molar mass distribution of the samples treated with electron beam in comparison with the control samples.

It was noticed the decrease of the molecular weights as the irradiation increase for both starches, indicating the degradation phenomenon of the macromolecules. The decreasing evolution of the molecular weights with the irradiation dose suggests the break of polymeric chain and formation of the fragments with different molecular weights, which modify the mass molecular distribution of each sample. Even $M_n$ and $M_w$ concomitantly decreased, though their evolution was differently influenced by irradiation and it was reflected by polydispersity index as well. The polydispersity decreased by e-beam treatment of corn starch showing the change of the molecular weight distribution, so that the $M_w$ decreased faster than $M_n$ with the irradiation dose. For potato starch, it was observed a slight increase of the polydispersity after e-beam treatment showing that $M_n$ decreased faster than $M_w$. The molecular fractions with low molecular weights appeared with a higher percentage than the fractions with high molecular weigh as a consequence of the e-beam treatment.

*Table 1*

**Molecular weight distributions of starch samples**

| Irradiation dose [kGy] | **$M_n$ x 10$^{-4}$ [g/mol]** | **$M_w$ x 10$^{-5}$ [g/mol]** | **$M_z$ x 10$^{-5}$ [g/mol]** | ***PI*** |
|---|---|---|---|---|
| *Corn starch* | | | | |
| 0 | **5.52 ± 0.45** | **3.07 ± 0.22** | **8.36 ± 0.31** | 5.56 ± 0.23 |
| 10 | **4.19 ± 0.14** | **2.34 ± 0.02** | **6.43 ± 0.03** | 5.58 ± 0.12 |
| 20 | **3.62 ± 0.37** | **1.78 ± 0.08** | **5.43 ± 0.02** | 4.92 ± 0.27 |
| 30 | **3.42 ± 0.21** | **1.50 ± 0.03** | **4.75 ± 0.12** | 4.41 ± 0.37 |
| 40 | **2.87 ± 0.03** | **1.16 ± 0.02** | **3.82 ± 0.10** | 4.04 ± 0.28 |
| 50 | **2.84 ± 0.13** | **1.12 ± 0.05** | **3.48 ± 0.39** | 3.95 ± 0.34 |
| *Potato starch* | | | | |
| 0 | **8.85 ± 0.04** | **4.41 ± 0.04** | **9.81 ± 0.06** | 4.98 ± 0.20 |
| 10 | **6.72 ± 0.54** | **3.67 ± 0.23** | **9.38 ± 0.17** | 5.46 ± 0.45 |
| 20 | **5.57 ± 0.44** | **2.98 ± 0.09** | **8.50 ± 0.28** | 5.35 ± 0.54 |
| 30 | **4.16 ± 0.11** | **2.22 ± 0.01** | **7.60 ± 0.08** | 5.33 ± 0.13 |
| 40 | **3.38 ± 0.15** | **1.83 ± 0.10** | **6.57 ± 0.07** | 5.40 ± 0.39 |
| **50** | 3.20 ± 0.14 | 1.73 ± 0.05 | 6.01 ± 0.23 | 5.41 ± 0.50 |

The results are mean values with standard deviation of two replicates.

To charaterize cantitatively the polymer radiodegradation process is generally used the degradation index *Id* [8-10], which represents the average number of scissions that occur in the initial molecule due to the radiation and it can be described by equation (1):

$$Id = \frac{M_0}{M} - 1 \tag{1}$$

where: $M_0$ – initial molecular weight,

$M$ – molecular weight of the polymer irradiated with the irradiation dose $D$.

Assuming that the rate of the polymeric chain break is independent of its length and branches, then the dependency of the degradation index, known as the degradation rate, on the irradiation dose is linear:

$$Id = k \cdot D \tag{2}$$

where: $k$ – degradation rate constant [kGy$^{-1}$],
$D$ – irradiation dose [kGy].

Consequently, the equation (1) can be rewrite as equation (3):

$$Id = \frac{M_0}{M} - 1 = k \cdot D \tag{3}$$

so that:

$$\frac{M}{M_0} = \frac{1}{1 + k \cdot D} \tag{4}$$

The rate constants $k_n$, $k_w$ and $k_z$ of the $M_n$, $M_w$ and $M_z$ degradation of both studied starches were determined by graphical representation of degradation index $Id$ as a function of the irradiation dose (Figs. 1 and 2).

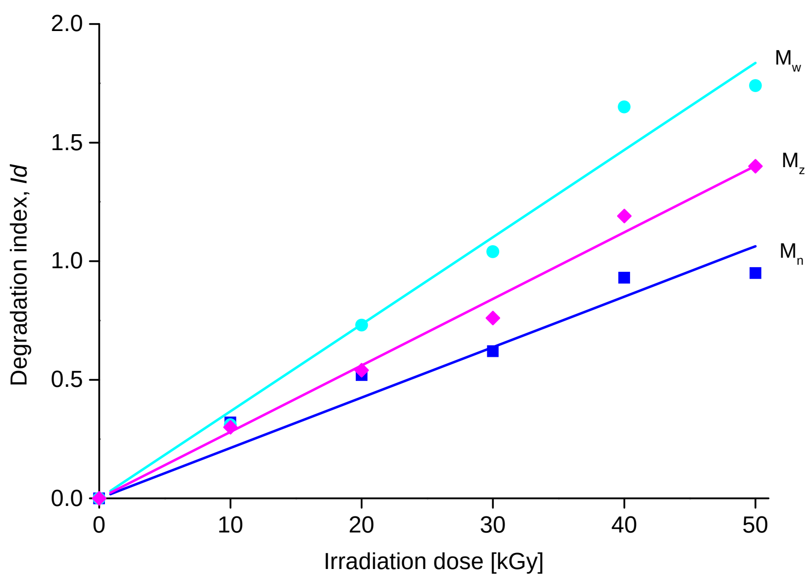


Fig. 1. Graphical representation of degradation index vs. irradiation dose of corn starch

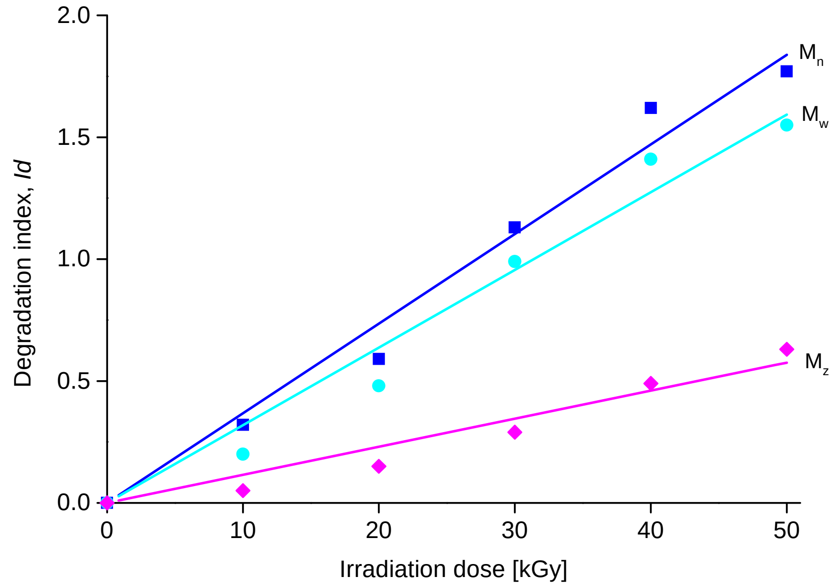


Fig. 2. Graphical representation of degradation index vs. irradiation dose of potato starch

The values of the determined are showed in Table 2.

*Table 2*

**Degradation rate constants**

| Starch | $k_n$ x 10³ [kGy⁻¹] | $k_w$ x 10³ [kGy⁻¹] | $k_z$ x 10³ [kGy⁻¹] |
|---|---|---|---|
| Corn | **21.25 ± 1.35** | **36.71 ± 1.49** | 28.04 ± 0.74 |
| **Potato** | 36.76 ± 1.52 | 31.85 ± 1.65 | 11.51 ± 0.89 |

If we take into account that the degradation rate is direct proportional with the rate constant, one can observe that the degradation rate is different for both the molecular fractions and starch type. Thus, based on the data presented in Table 2, it can be noticed that the number molecular fraction is preponderantly affected for potato starch, meaning that the fractions with low molecular weight are firstly degradated, while the weight molecular fraction is especially affected for the corn starch.

The radiodegradation rate evolution for both investigated starches was different and it could be influenced by the different structural organization of these starches, especially due to the amylopectin which has a complex branched structure, characterized by short chains for corn starch and longer chains for potato starch.

## 4. Conclusion

The starch structure type influenced the evolution of molecular weight with the irradiation dose. Thus, for con starch with short chains, the molecular weight distribution was affected especially by the formation of fraction with higher molecular weight than the formation of fraction with low molecular weight. For potato starch with long chains, the molecular weight distribution is only slightly changed by e-beam treatment, the scissions in fractions with high molecular weight being closer to that of the fractions with low molecular weight.

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