Physico-chemical and Structural Characterization of Corn Starch Modified by Combined Electron Beam with Microwave Treatment

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The paper presents the experimental results regarding the investigation of some physico-chemical and structural characteristics of starch modified by electron beam and microwave combined treatment. The combined electron beam (EB) and microwave (MW) treatment of granular starch was performed in four different regimes, successive and simultaneous. The experimental data showed that the acidity of starch aqueous solutions increased while the apparent viscosity reduced as a function of the treatment parameters and regime. No significant changes appeared in the morphological characteristics of the samples treated with combined EB-MW, but the spectral characteristics suffered minor changes suggesting that the stability of hydrogen inter- and intramolecular bonds is affected. At the same time, the degree of order increased after successive combined treatments indicating some molecular associations or rearrangements in amorphous component of starch due to the microwave field. The evolution of the molecular weights and molecular weight distribution indicated that the macromolecular degradation cannot be correlated with the specific absorbed energy as a consequence of the microwave field contribution.

Keywords: starch, electron beam, microwave, viscosity, SEM, GPC

Starch is a macromolecular compound used in plastics industry to improve the biodegradability. Due to its abundance and low cost, starch is one of the most promising biopolymers for use in biodegradable plastics [1]. It is used as filler in synthetic polymers, it is blended on a micro-scale with synthetic polymers or it is mixed with polyols to form a thermoplastic amorphous mass [2].

The native form of starch is generally subjected to some modifying treatments in order to extend its applications. These treatments can be physical, chemical, enzymatic or even combinations of these types. A great importance was showed lately to the development of ecological, fast and low cost methods of starch treatment like electron beam treatment which is already applied at industrial scale. Thus, an innovative treatment combining electron beam and microwave field could bring economical benefits and the possibility to extend the range of starch-based products. Electron beam treatment causes the degradation of starch macromolecular structure, which can change its physico-chemical and structural properties leading to the increase of solubility, reduction of swelling power, viscosity and gelatinization temperature of starch pastes [3-6] as a function of irradiation dose. Microwave treatment determines the rearrangement of starch molecular structure indicating that the starch granule structure is disintegrated, which leads to a slight reduction of both water absorption ability, solubility and swelling power, as well as changes of paste gelatinization temperature and viscosity [7-10] correlated with the experimental parameters of treatment.

The aim of this paper consists in the investigation of some physico-chemical and structural properties of starch subjected to combined electron beam and microwave treatment.

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Experimental part

Corn starch having 10.9 wt% moisture content from Romanian market was used for the experiments.

Combined EB-MW treatment was carried out using an installation which consists in an accelerated electron source, a microwave generator and a multimode rectangular cavity (INFLPR, Bucharest-Magurele, Romania). Powder starch samples disposed in cryovial tubes PP 309 2A were treated at ambient temperature and normal pressure. The tube caps were removed before treatment, being put back in the end of the treatment.

Combined EB-MW treatment was applied in four different regimes:

- successive: electron beam followed by microwaves (EB/MW),
- successive: microwaves followed by electron beam (MW/EB),
- simultaneous: electron beam and microwaves (EB + MW),
- partially simultaneous electron beam and microwaves (EB + MW partial).

The used irradiation dose was 3 kGy with a dose rate of 2 kGy/min, the values of microwave powers were 450, 750 and 2540 mW, for different treatment times (14 – 270 s).

*p*H was measured for 1% aqueous solutions of starch at 25°C with a Denver pH-conductivity meter (Denver Instruments, USA).

The rheological measurements were carried out on 5% aqueous starch suspensions using a rotational HAAKE VT® 550 viscometer (ThermoHaake, Germany) with NV coaxial cylinder. The shear stress, τ and apparent viscosity, η_a of the samples were measured at 25°C for different shear rates, $\dot{\gamma}$. The obtained data were analyzed with RheoWin v. 3.5. software.

Microwave power [mW]	Treatment time [s]	Treatment regime			
		EB/MW	*MW/EB*	*EB+MW*	*EB+MW partial*
0	0	7.7 ± 0.1 *(control sample)*			
		7.6 ± 0.2 *(3 kGy)*			
450	189	6.9 ± 0.2	6.5 ± 0.1	-	-
	230	7.0 ± 0.2	6.8 ± 0.3	-	-
	270	7.0 ± 0.1	6.9 ± 0.1	-	-
750	67	7.1 ± 0.1	6.8 ± 0.1	-	6.8 ± 0.2
	74	6.7 ± 0.1	6.4 ± 0.1	-	6.6 ± 0.1
	78	6.7 ± 0.1	6.5 ± 0.2	-	6.6 ± 0.1
	82	6.6 ± 0.1	6.4 ± 0.1	-	6.5 ± 0.1
	86	6.4 ± 0.1	6.3 ± 0.1	6.4 ± 0.1	-
2540	14	6.9 ± 0.1	7.0 ± 0.3	-	-
	16	6.6 ± 0.1	6.9 ± 0.2	-	-
	18	6.8 ± 0.2	6.8 ± 0.2	-	-

Table 1
*p*H VALUES OF THE AQUEOUS SOLUTIONS OF STARCH MODIFIED BY COMBINED EB-MW TREATMENT

The analysis of starch granules by scanning electron microscopy (SEM) was performed using a FEI Nova™ NanoSEM 630 microscope.

FTIR spectra were recorded on a FTIR Tensor 27 spectrometer (Bruker Optik GmbH, Germany) in the frequency range of 4000 – 400 cm^{-1} using KBr discs prepared from powdered samples mixed with dry KBr.

The samples for GPC analysis were prepared according to the method described [11] slightly modified. Thus, starch (10 μg) was wetted with ethanol (20 μL), and then dispersed in 1M NaOH (500 μL). The mixture is then magnetically stirred (1000 rpm) for 10 min at 35^0 C. The starch solution obtained was diluted to 50mM NaOH with water and gently stirred again (150 rpm) for 30 min 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.

Results and discussion

Aqueous starch solution had relative neutral *p*H that decreased with the irradiation dose increase by EB treatment [12]. Though a relative low irradiation dose of 3 kGy led to insignificant change of *p*H value as it can be seen in Table 1, the combined EB-MW treatment, applied in all four regimes, caused an important decrease of *p*H value. This result suggests that starch subjected to combined EB-MW treatment suffered a degradation phenomenon which led to formation of chemical groups with acidic character.

It can be observed that the most reduced *p*H values were obtained for combined MW/EB treatment with low microwave powers of 450 and 750 mW. Therefore, for the microwave power of 750 mW, the *p*H value decreased with the increase of treatment time, while for lower microwave power of 450 mW, the *p*H value decreased suddenly for the treatment (189 s/3 kGy) increasing then slightly with the increase of treatment time, but remaining under the *p*H value of the control sample.

EB/MW regime treatment with microwave power of 750 mW led systematically to the reduction of *p*H value as the treatment time increases, but less than for MW/EB regime. Simultaneous or partial EB+MW regime, applied with microwave power of 750 mW, determined the *p*H decrease slightly smoother than MW/EB regime, but more pronounced than EB/MW regime.

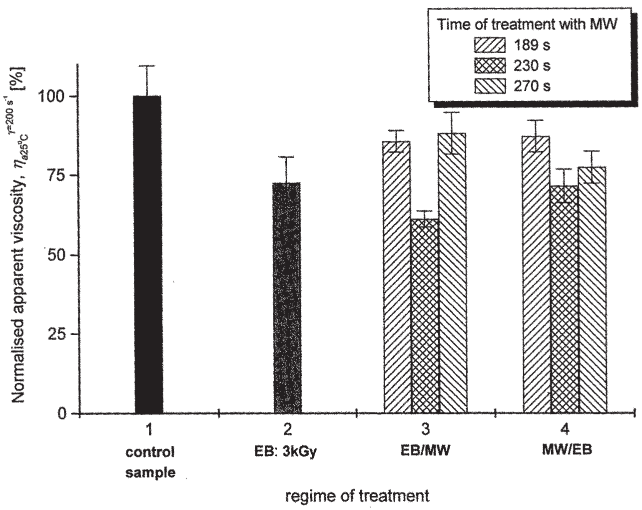

Fig. 1. The effect of the combined EB-MW treatment, with microwave power of 450 mW, on the apparent viscosity of corn starch suspensions

Corn starch forms aqueous suspensions with non-Newtonian behaviour having pseudoplastic behaviour [13] and EB treatment with doses over 10 kGy affects this behaviour [12], determining a tendency to become a Newtonian one with the increase of irradiation dose. However, EB treatment with 3 kGy affected insignificantly the non-Newtonian behaviour of starch aqueous suspension. Combined EB-MW did not affect also the rheological behaviour of corn starch aqueous suspension which kept the increasing evolution of shear stress τ with the increase of shear rate $\dot{\gamma}$, typical to a fluid pseudoplastic behaviour.

The apparent viscosity (25^0 C, $\dot{\gamma}$=200 s^{-1}) of aqueous suspension of starch shows generally decreasing evolution as the irradiation dose increases [5]. It can be noticed that in case of corn starch aqueous suspension, the irradiation dose of 3 kGy caused the viscosity decrease of approximately 27% from initial value.

The suspensions of starch treated both in EB/MW and MW/EB regime, with microwave power of 450 mW, showed variable values of viscosity as function of microwave treatment time and applied combined treatment regime (fig.1). It can be observed that the viscosity of all treated samples is more or less around the value obtained for the samples treated with EB at 3 kGy. For the same treatment parameters, power and time, the viscosity values depend on treatment regime, but it can be noticed that the minimum value of viscosity was obtained for the same treatment time in both treatment regimes.

Combined treatment of starch, with microwave power of 750 mW, led to a minimum value of viscosity for each treatment regime, having lower values than viscosity value of the sample treated with EB at 3 kGy (fig. 2). In this case, it can be observed that the value of the extreme was achieved for different treatment times, so that, for instance, an extreme was achieved for treatment time of 78 s applying EB/MW regime, while applying MW/EB treatment, the extreme was achieved for treatment time of 82 s.

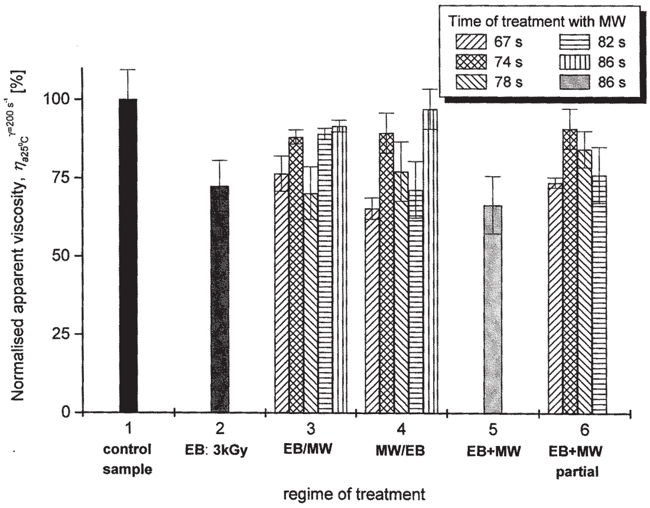

Fig. 2. The effect of the combined EB-MW treatment, with microwave power of 750 mW, on apparent viscosity of corn starch suspensions

As a consequence of the combined treatment with microwave treatment of 2540 mW, the lowest viscosity values were obtained for EB/MW regime. On the contrary, the viscosity values varied insignificantly for MW/EB regime and those three treatment times. Due to the very short and close time values of the microwave treatment, a minimum value cannot be achieved, though lower viscosity values than that of the sample treated with EB at 3 kGy (fig. 3) were obtained.

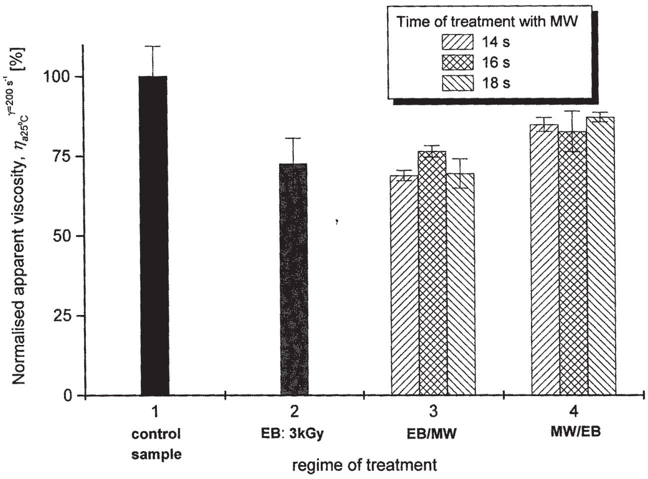

Fig. 3. The effect of the combined EB-MW treatment, with microwave power of 2540 mW, on apparent viscosity of corn starch suspensions

All obtained results show that the combined EB-MW treatment, in our experimental conditions, led to the apparent viscosity reduction depending on both microwave power, time and treatment regime. This reduction could suggest a degradation of the starch macromolecule similar to that produced by EB treatment [3-5]. Though, for the combined treatment case, the degradation degree cannot be correlated with the treatment parameters, while the effects of EB treatment can be correlated with the irradiation dose. This aspect is certainly due to the contribution of microwave field determining the properties of starch subjected to this field to evolve unpredictably. In addition, for the same microwave power and treatment time, the apparent viscosity values varied as function of treatment regime (EB/MW, MW/EB or EB+MW) supporting the principle that the effect of the combined treatment is not the sum of the effects of EB and MW treatments considering that each of these two treatments would influence separately the starch macromolecule.

The experimental results obtained by SEM investigation showed that corn starch (fig. 4a) has granules with polyhedral shape, slightly roughened surface and rarely concave, having tendency to agglomerate as a bunch and presenting occasionally small holes on some granule surfaces.

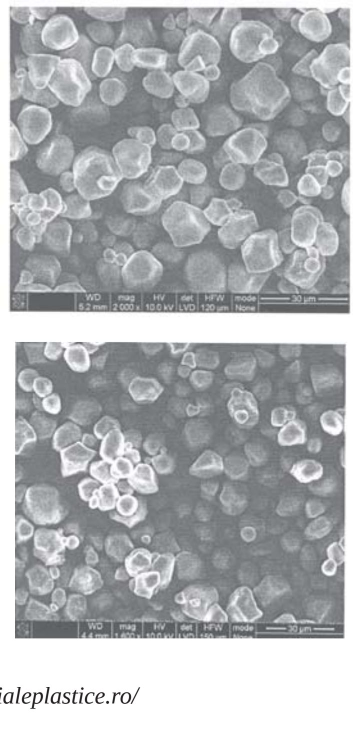

Fig. 4. SEM images of corn starch granules for: (a) control sample and (b) sample treated with 3 kGy

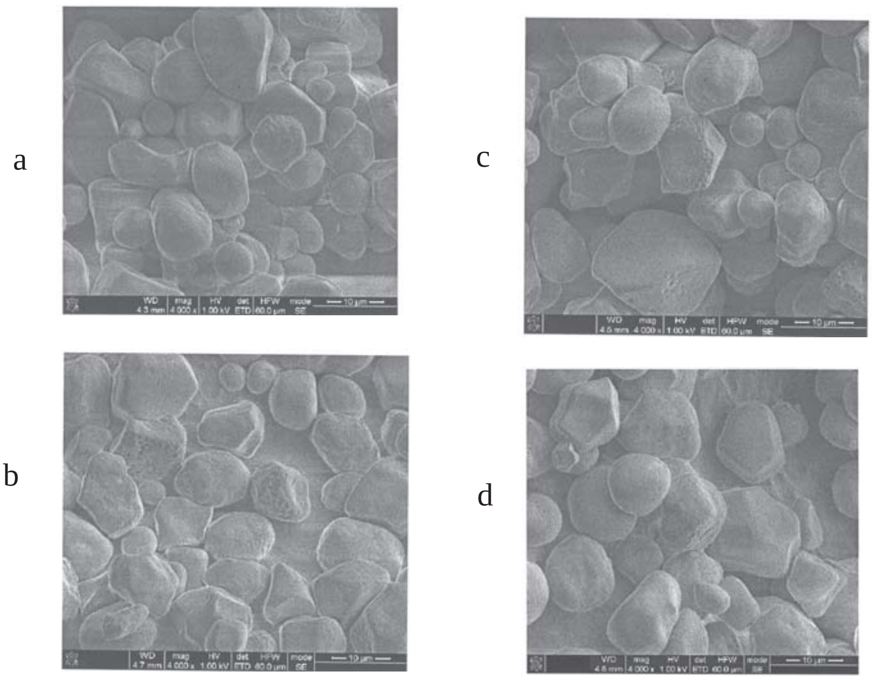

Fig. 5. SEM images of corn starch treated with: (a) (450 mW, 270 s)/3 kGy, (b) (750 mW, 86 s)/3 kGy, (c) 3 kGy+(750 mW, 86 s) and (d) 3 kGy/(2540 mW, 18 s)

Electron beam treated corn starch had granules that are less agglomerated than control sample, their shape and sizes being unaffected apparently. However, it can be observed the appearance of small circular "lesions" on granule surface. Figure 4b shows the SEM micrograph of 1600x for corn starch treated with electron beam at irradiation dose of 3 kGy.

The combined EB-MW treatment, independently of the treatment regime, did not alter considerably the granule morphology (fig. 5). Even though, the shape of granules seemed to be more rounded, and the surface appeared more roughened as compared to control sample.

Some studies concerning the microwave treatment of starch [7,14] describe the appearance of either some cracks or central indentations on the granule surface which contribute to granule deformation, or a slight change of the granule shape, depending on experimental conditions. The experimental conditions considered for our study slightly modified the granule aspect, but no cracks, indentations or other kind of "lesions" were caused on the granule surface.

In order to discuss the spectral characteristics of the starch subjected to EB-MW treatment, the spectroscopic bands specific for IR range were identified in the first stage, then the crystalline level was determined and thus the influence of treatment applied on starch was revealed.

The spectral characteristics of the corn starch treated with combined EB-MW (fig. 6) were similar to the native starch, independently of treatment parameters and regime. Slight shifts of some peaks were identified for samples treated with combined EB-MW as well as sample treated with EB, but they do not indicate any significant change in the starch structure.

These minor changes that appeared mainly for bands attributed to C-H and O-H bonds can be associated with the intensity and stability of these bonds, suggesting that the combined EB-MW treatment affects the stability of inter- and intramolecular hydrogen bonds, but without any correlation with treatment parameters or regime.

In order to evaluate the order or cristallinity degree of starch treated with combined EB-MW, there were analyzed the bands obtained at approximately 1047 and 1022 cm^{-1} for which both a spectrum deconvolution in the range 950 – 1130 cm^{-1} and the ratio of the absorbance intensity of two kind of regions, crystalline/amorphous, were performed. The starch amorphous region is characterized

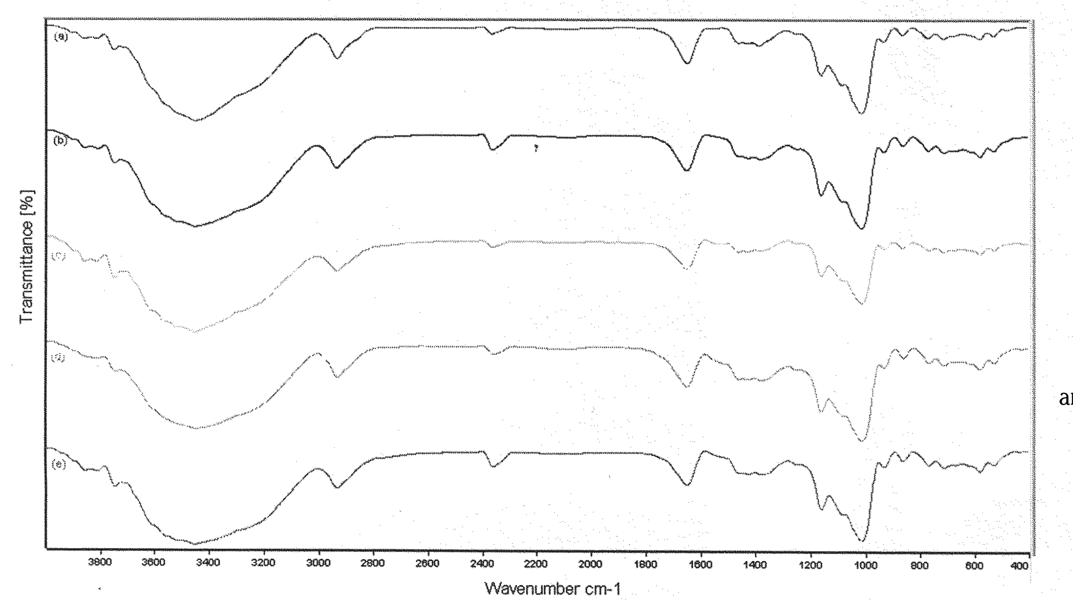

Fig. 6. FTIR spectra of corn starch (a) native form and treated with: (b) 3 kGy, (c) (450 mW, 230 s)/3 kGy, (d) 3 kGy+(750 mW, 86 s) and (e) 3 kGy/(2540 mW, 14 s)

Treatment regime	Irradiation dose [kGy]	Microwave power [mW]	Treatment time [s]	Amorphous	Crystalline	Band ratio 1047/1022
Control sample	0	0	0	1018	1054	0.46 ± 0.01
EB	3	0	0	1022	1053	0.47 ± 0.02
EB/MW	3	450	230	1022	1053	0.51 ± 0.01
EB/MW	3	750	78	1022	1053	0.50 ± 0.01
EB/MW	3	2 540	14	1022	1053	0.51 ± 0.01
MW/EB	3	450	230	1022	1053	0.49 ± 0.01
MW/EB	3	750	67	1022	1053	0.51 ± 0.01
EB+MW	3	750	86	1021	1053	0.46 ± 0.01

Table 2
ASSIGNATION OF BANDS CORRESPONDING TO 1022 cm^{-1} (AMORPHOUS REGION) AND 1047 cm^{-1} (CRYSTALLINE REGION), OBTAINED BY DECONVOLUTION OF SPECTRUM, AND BAND RATIOS 1047/1022

Microwave power [mW]	Treatment time [s]	Treatment regime: *EB/MW*	*MW/EB*	*EB+MW*
		***M_n/M_{n0}* [%]**		
0	0	100 *(control sample)*		
		94 *(3 kGy)*		
450	230	108	97	-
750	67	-	102	-
	78	99	-	-
	86	-	-	104
2540	14	95	-	-
		***M_w/M_{w0}* [%]**		
0	0	100 *(control sample)*		
		92 *(3 kGy)*		
450	230	86	89	-
750	67	-	86	-
	78	90	-	-
	86	-	-	87
2540	14	87	-	-
		***M_z/M_{z0}* [%]**		
0	0	100 *(control sample)*		
		94 *(3 kGy)*		
450	230	90	87	-
750	67	-	91	-
	78	92	-	-
	86	-	-	87
2540	14	91	-	-
		PI		
0	0	5.56 ± 0.20 *(control sample)*		
		5.44 ± 0.11 *(3 kGy)*		
450	230	4.39 ± 0.09	5.13 ± 0.14	-
750	67	-	4.70 ± 0.19	-
	78	5.05 ± 0.14	-	-
	86	-	-	4.65 ± 0.10
2540	14	5.11 ± 0.12	-	-

Table 3
MOLECULAR WEIGHT DISTRIBUTIONS OF STARCH SAMPLES TREATED BY COMBINED EB-MW METHOD

by an absorption band around 1022 cm^{-1} while the crystalline state can be identified by appearance of a band at 1047 cm^{-1} [15-17].

Thus, based on the experimental data, the bands correlated with the amorphous region and crystalline state, respectively, were identified. In table 2 the identified bands and ratios of absorbance intensities of these two regions, that were used to quantify the order/cristallinity degree of starch are shown.

The increase of the order/cristallinity degree which can be observed after the combined treatments of starch is rather due to some molecular associations or rearrangements in the amorphous component of starch granule than to a so-called crystallization that occurred after microwave treatment for different starches [8].

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 combined EB-MW treatment on molecular weights and distribution.

Table 3 shows the molar mass distribution of the samples treated with combined EB-MW in different experimental conditions in comparison with the native and 3 kGy irradiated starch samples.

For all samples treated with combined EB-MW, independently of treatment parameters and regime, it was noticed the decrease of M_w and M_z molecular weights in comparison with the control sample. These molecular weights were also systematically lower than the corresponding molecular weights of the sample irradiated with 3 kGy, but with values relatively close to this one. Such evolution indicates a possible degradation phenomenon of starch macromolecule leading to the formation of fragments with different molecular weights. This phenomenon did not show any obvious dependence on the experimental conditions. However, the M_n values of the samples treated with combined EB-MW varied around the values of the same control sample mass fraction, increasing or decreasing, but with higher values than the value of the 3 kGy irradiated sample. Obviously it can be observed that the M_w and M_z values were influenced in the same direction by combined treatment as the EB treatment, while the M_n was affected in the opposite direction compared to the EB treatment.

The M_w value decreases as the increase of M_n value led to a decreasing evolution of polydispersity after combined EB-MW treatments (table 3), even more than EB treatment where the polydispersity decrease was possible because M_w was rather affected than M_n. This kind of behavior shows that the microwave field, having a different interaction mechanism with matter than electron beam, is able to break up small fragments from the macromolecule so leading to the increase of the number of the fractions with low molecular weight, without affecting dramatically the other molecular weights.

Conclusions

The combined EB-MW treatment, applied in all four studied regimes and the selected experimental conditions, induced changes of some physico-chemical properties and structural characteristics of corn starch. In these conditions, the combined treatment led to a degradation phenomenon of starch macromolecule, which was not correlated directly with treatment parameters so that the properties of the starch subjected to the irradiation fields behaved unpredictably. In addition, for the same irradiation dose, microwave power and treatment time, the values of a property may vary as a function of regime treatment (EB/MW, MW/EB or EB+MW) sustaining the principle that the combined treatment effect is not the sum of the effects of EB and MW treatments considering that each of these two treatments would influence separately starch macromolecule.

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