Controlling of Degradation Effects in Radiation Processing of Starch

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Controlling of Degradation Effects in Radiation Processing of Starch

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Corn starch of different physical forms (solid and liquid) was irradiated with ^{60}Co gamma rays and electron beam in the dose range of 50 Gy to 100 kGy to investigate the effect of ionizing radiation on its molecular weight (M_w). Degradation was observed for both solid and liquid states upon radiation. However, degradation of the starch in the liquid state was remarkably greater than that in the solid state. The free radicals that formed during water irradiation must be responsible for such degradation in the liquid form. Thermostated viscometer, rheometer and multi-angle static laser light scattering were employed to study the changes in the M_w of corn starch that occurred during irradiation at constant temperature and different concentrations. It was observed that electron beam irradiated corn starch has uniform decreasing in M_w and radius of gyration (R_g) in the range of (4.4×10^7–2.9×10^7 g mol^{-1}) and (199.3–85.6 nm), respectively. The influence of gas atmosphere on the degradation process during gamma irradiation was studied to find that, the M_w and R_g values were in the range of (4.4×10^7–1.8×10^7 g mol^{-1}) and (199.3–120.4 nm) for the oxygen saturated samples, while, they were (4.4×10^7–1.05×10^7 g mol^{-1}) and (199.3–85.6 nm) for the argon saturated samples.

Keywords: radiation; starch; degradation

1 Introduction

Starch and glycogen are storage polymers of glucose in plants and animals, respectively. Starch is the most abundant dietary carbohydrate in cereals, potatoes, legumes, corn and other vegetables. It is generally a mixture of linear and branched components. The linear component shaped in the form of a helix amylose, is the minor component, that ranges from 20 to 30% and has a molecular weight of several hundred thousands. The branched component, amylopectin, is the major component, which has molecular weight in the order of several millions. The average chain-length of amylopectin is about 20−30 glucose units. It is composed of short alpha [1,4]-linked chains connected to each other by alpha [1,6]-glucosidic linkages (1). Branch chains in amylopectin are arranged in clusters, and are present in double helical crystalline structures (2). Starch is a natural, biodegradable polymer because it can be readily metabolized by a wide array of organisms (3). Viscosities of native starch gels are often too high for industrial applications and there is a need for efficient methods of reducing them to the desirable level (4). Researchers have been focused mainly on non-digestible oligosaccharides and resistant starch (5). Degradation of starch is one among the common targets of starch processing. It provides a wide spectrum of products from white (thin-boiled) through yellow dextrins up to D-maltose and D-glucose (6). Starch hydrolysis products are industrially produced by enzyme reactions from a dissolved solution of starch (7). Since the average chain length of natural polysaccharides is determined by their source of origin and in most cases, it cannot be influenced, there is a need for a fast, efficient, and inexpensive method of processing the native polysaccharide substrates in order to achieve the desired average molecular weight or the desired molecular weight distribution. Chemical treatments, that involve the use of chemicals and generates waste, for example acid hydrolysis, is often time and energy consuming. Moreover, it is not always easy to control a multi-parameters process, although considerable progress in this technique has been achieved (8−11).

Polysaccharides are typical radiation-degradable materials. This manifests itself as a reduction of average molecular

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weight upon irradiation (12, 13). The irradiation of starch could be with different sources of energy such as neutrons, X-ray, high-energy electrons, gamma-rays, visible and ultraviolet light, infrared radiation, microwave radiation, ultrasound, silent electrical discharge, pressure treatment (extrusion) and heat moisture (14). Starch degradation was studied to find that chemical and structural changes are provoked by gamma irradiation (15).

The aim of this work is to provide quantitative data on the ionizing radiation that induced degradation of starch, as natural polymer in the solid and liquid forms.

2   Experimental

2.1   Materials

Corn starch was supplied by Sigma. All other chemicals were reagent grade and used as received.

2.2   Preparation of the Starch Solution

Completely dispersed 5% starch solution is a prime requisite to deal with molecular weight determination. To prepare the starch solution, 5 g of starch were dispersed in 10 ml of 0.5 N sodium hydroxide, followed by neutralization to pH 7 by the addition of perchloric acid and then the mixture was diluted with distilled water to 100 ml. The starch specimens were packed and irradiated as a solid powder in polyethylene bags and as liquid in glass bottles. Aqueous solutions were made up of water purified by the Nanopure II system (Barnstead, USA). Viscosity measurements were carried out at a temperature of $25.0 \pm 0.1°C$ using an AVS-350 setup (Schott Geräte) equipped with an Ubbelohde viscometer. UV spectra of starch solutions were recorded by the use a Perkin−Elmer Lambda 40 UV/Vis spectrophotometer.

2.3   Degradation of Starch by Gamma-Rays

Two gamma ^{60}Co sources were used for this purpose. The starch specimens were exposed at ambient temperature (20 ± 0.5) to a gamma ^{60}Co source (1.17−1.33 MeV) of total activity 18.000 Ci and dose rate 3.2 kGy/h. The dose levels applied to the samples were 5−100 kGy. Another gamma ^{60}Co source with six movable columns with cavities for sample placement, electrical control, irradiation power in a single niche 90 Gy/h. with a rotary tray was used. The dose levels applied to the Ar and O_2 saturated starch solutions were 100−1600 Gy.

2.4   Degradation of Starch by Electron Beam

The starch specimens were subjected to pulse irradiation with 6 MeV electrons from an ELU-6E linear accelerator (Eksma, Russia) which was installed at the Institute of Applied

Radiation Chemistry, Technical University of Lodz, Poland. The dose levels applied to the sample were 5−100 kGy.

2.5   Determination of Viscosity-Average Molecular Weight

Viscometry was used to obtain the viscosity-average molecular weight (M_v). The intrinsic viscosity [**η**] is proportional to the ratio of the effective volume of the molecule in solution divided by its molecular weight (16). The intrinsic viscosity can be related to the average molecular weight of a polydispersed polymer by the Mark−Houwink−Sakurada equation (17).

$$[\eta] = K(M_v)^a$$

where: M_v is the average molecular weight of the polymer which is viscometrically measured, K is a constant which depends on the polymer chemical composition, a is a constant which depends on polymer−solvent interactions. Ideally, [K and a] are independent of polymer molecular weight or concentration (18). However, in practice, the values of K for calculating a number average molecular weight or a mass average molecular weight are greatly influenced by the polydispersity of the sample (17).

2.6   Determination of Apparent Viscosity

Viscosity may be defined mathematically by this formula:

$$\eta = \frac{t}{D}(Pa \cdot s)$$

Where: η is the apparent viscosity, **t** is the shear stress and D is the rate of shear. Viscosity measurements would express in "Pascal seconds" (Pa · s).

2.7   Determination of Weight-Average Molecular Weight and Radius of Gyration

There are two types of light-scattering (LS (measurements, dynamic and static light-scattering (DLS and SLS, respectively). The foundation of DLS is based on the scattering of light by moving particles. In SLS, the intensity of scattered radiation is averaged over a fairly long time (≈ 2 s), and this is, in most cases, long enough to smooth out all internal mobility (19). SLS gives information about the weight average molecular weight (M_W) and average radius of gyration, (R_g) of macromolecules in dilute solution (20). M_w and R_g values of various species of starch using a light scattering technique were reported (21).

In our study, the weight-average molecular weights and radius of gyration R_g were determined by multi-angle laser light-scattering on a BI-SM 200 setup (Brookhaven Instruments) equipped with a Innova 90C argon ion laser (N = 514.5 nm). Starch was analyzed in solutions of pH 7 containing 0.25 mol dm^{-3} of sodium perchlorate. The refractive index increment for starch in 0.5 N NaClO$_4$ solution was taken as dn/dc = 0.146 cm^3 g^{-1} (22). The starch solutions

were passed through filters (Minisart, Sartorius) of 0.45 μm pore size before the light-scattering measurements. Intensity of the scattered light was measured for at least 5 dilutions of each sample in the angular range 30−135°. Zimm-plot algorithm was applied for the evaluation of results (23).

3 Results and Discussion

3.1 Effect of Physical Form of Starch on its Degradation

Starch of different physical states (solid and liquid) and different concentrations was irradiated at ~25°C with ^{60}Co gamma rays to investigate the effect of radiation on its degradation and the results are shown in Figure 1.

It can be seen that the reduced viscosity of unirradiated starch is higher than that of the irradiated one and it increases with starch concentration because of the increase in hydrogen bonding with hydroxyl groups and the distortion in the velocity pattern of the liquid by hydrated molecules of solute. It is also observed that at given concentration, the viscosity markedly decreases upon irradiation of starch in liquid form due to the attack of OH radicals on starch macromolecule leading to scission of 1−4 glycosidic bonds that is
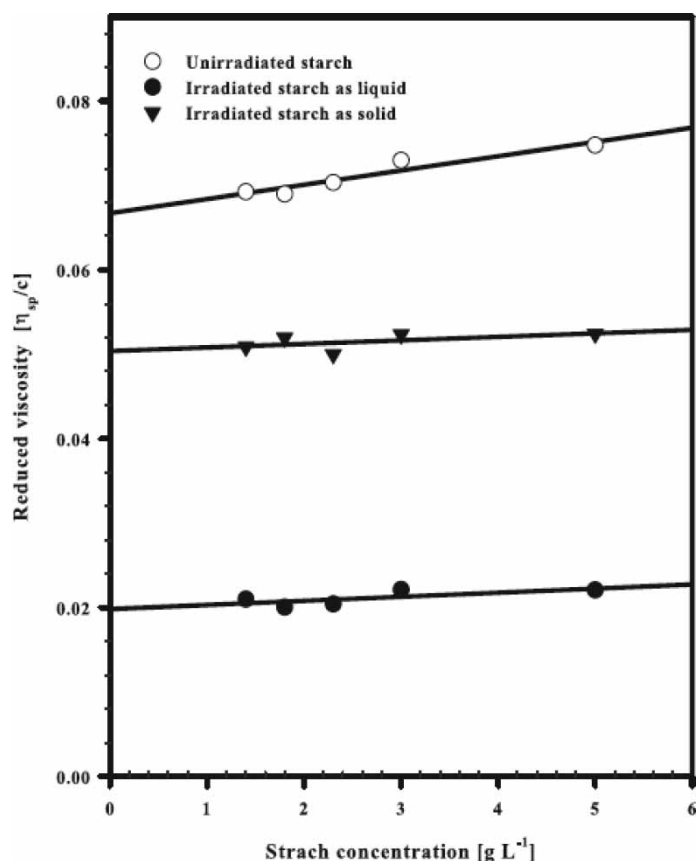
equivalent to chain scission (24). An extrapolation to the zero concentration would yield one, single value noted as intrinsic viscosity. The intrinsic viscosity values of unirradaited starch, 5 kGy irradiated as a powder and 5 kGy irradiated as liquid were found to be $6.667e^{-2}$, $5.036e^{-2}$ and $1.979e^{-2}$, respectively.

3.2 Effect of Irradiation Dose on Intrinsic Viscosity and Viscosity-Average Molecular Weight

Figures 2 and 3 show the effect of total absorbed dose on the intrinsic viscosity and viscosity average molecular weight, respectively. The quantitative assessment of molecular weight changes of starch irradiated samples were based on estimation of their viscosity-average molecular weights (M_v) using the Mark-Houwink relationship:

$$[[\eta] = K(M_v)^a]$$

Where: K, a are parameters for specific polymer, solvent and temperature. The reported parameters were $K = 1.44 \times 10^{-5}$ cm^3 g^{-1}, a = 0.93 (1). The results demonstrated that the intrinsic viscosity and M_v of gamma irradiated starch was considerably decreased with increasing irradiation

Fig. 1. Effect of starch concentration on its reduced viscosity. Temperature; 25°C, irradiation dose; 5 kGy, dose rate; 3.2 kGy/h.
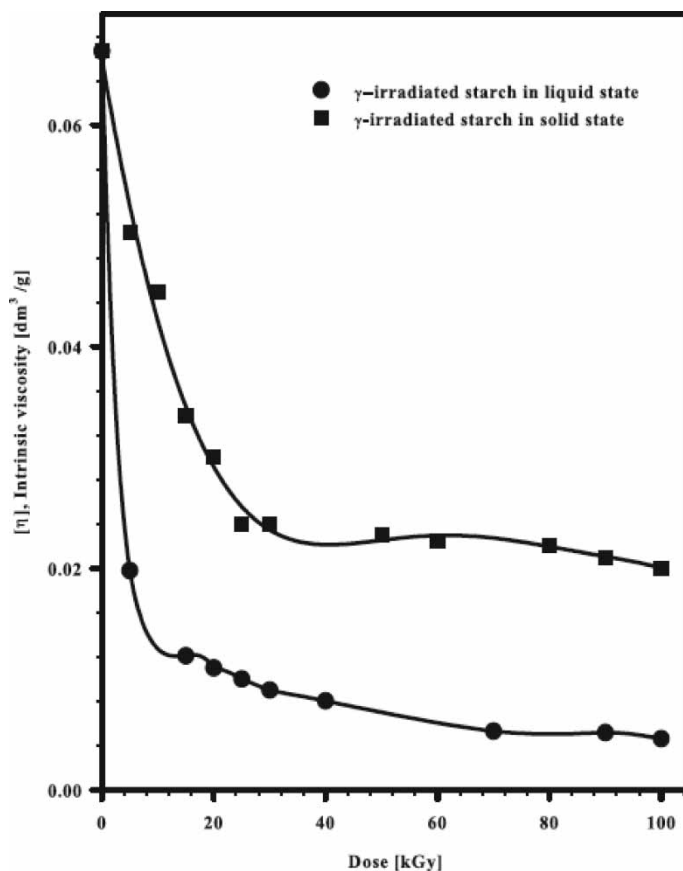

Fig. 2. Intrinsic viscosity of starch [η] as a function of total absorbed dose. Irradiation dose rate; 3.2 kGy/h, Starch concentration; 5 g L^{-1} in aqueous solution containing 5×10^{-2} mol dm^{-3} NaClO$_4$.
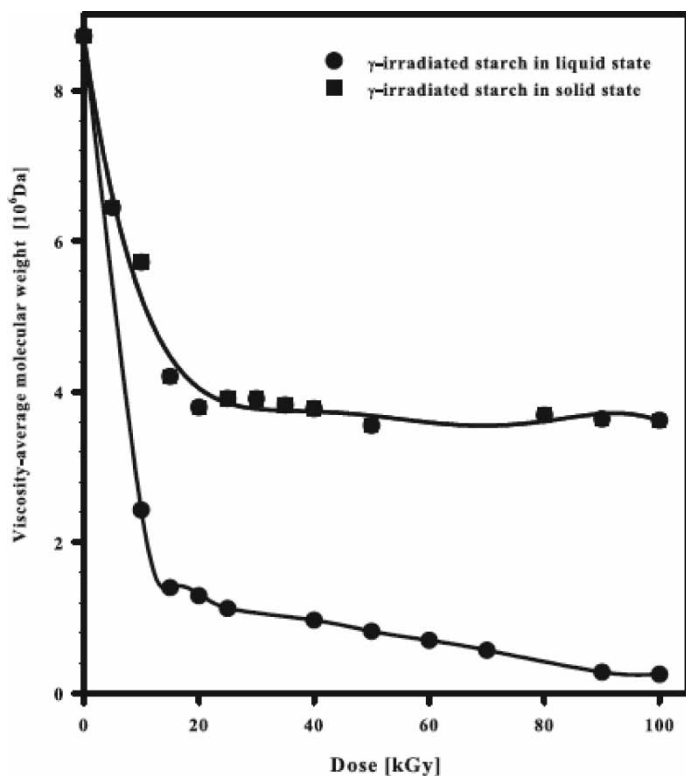
Fig. 3. Viscosity-average molecular weight of starch as a function of total absorbed dose. Mark-Houwink Parameters: $K = 1.44 \times 10^{-5}$ cm^3 g^{-1}, a = 0.93, temperature; 25°C, dose rate; 3.2 kGy/h.

Fig. 4. Effect of shear rates on the apparent viscosity of starch irradiated as solid by gamma rays with different total doses, starch concentration for Viscosity measurements; 50 g L^{-1} in aqueous solution containing 5×10^{-2} mol dm^{-3} NaClO$_4$, dose rate; 3.2 kGy/h.

dose levels. A rapid decrease in the intrinsic viscosity and M_v were observed up to 15 kGy for both the solid and liquid forms, thereafter, the reduction in intrinsic viscosity and M_v slowed down gradually. A similar initial decrease of viscosity for irradiated wheat starch has been reported (25).

The results indicated that the higher the irradiation dose, the more the free radicals induced degradation of starch, and the lower the viscosity average molecular weight. Similar behavior for the irradiated wheat and corn starch was reported (26). Degradation of starch i.e., decrease in the molecular weight has been considered to be responsible for the viscosity changes caused by γ-irradiation depending upon the irradiation dose levels (27).

3.3 Effect of Ionizing Radiation Source on Starch Degradation

Starch exhibits unique viscosity behavior with a change of temperature, concentration and shear rate. This can be measured by a shearing device (rheometer). The apparent viscosity at different rates of shear for unirradiated, gamma and electron beam irradiated starch samples are shown in Figures 4 and 5. The results indicated that at a given rate of shear, the apparent viscosity decreases significantly on increasing the irradiation dose and the greatest decrease occurs in the initial stages of irradiation. For a given irradiation dose, the
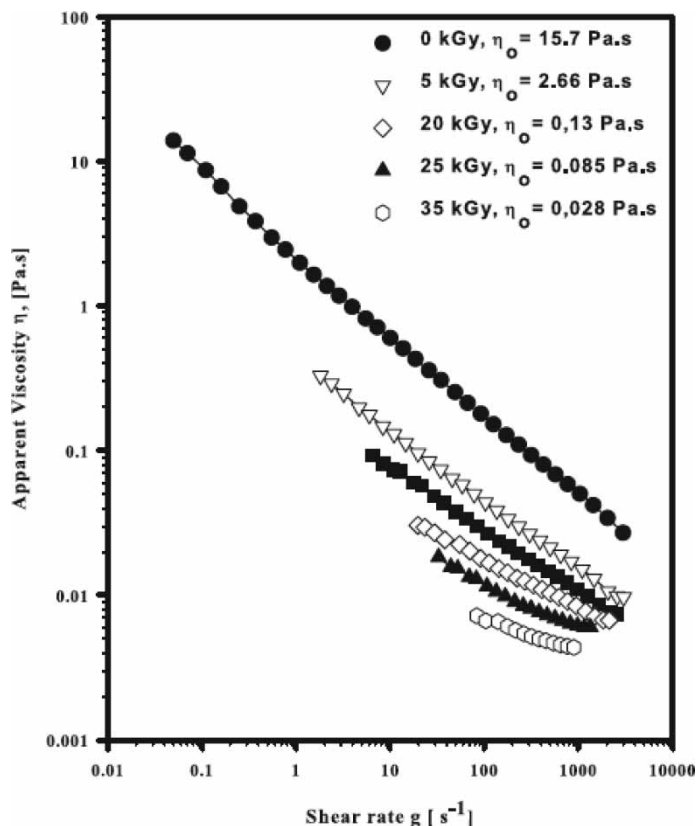
values of apparent viscosities decrease on increasing the rate of shear.

It is well known that, the light scattering is very sensitive to even small amounts of very high molecular weight fractions (real molecules and aggregates). Figures 6 and 7 show the molecular weight changes caused by the electron beam and gamma rays. According to the viscosity-average molecular weight, the electron beam modification of corn starch resulted in significantly lower disintegration compared to gamma irradiation, which may be due to the high penetration of γ-rays. Although, the light scattering results of gamma irradiated starch (Figure 7) revealed that there are some kinds of aggregations which occurred at the early stages of irradiation at which the M_w increases with dose. However, the continuous increase of irradiation dose causes fragmentation of the starch molecules, while viscometry does not. By its nature, viscometry gives values closer to the number-average molecular weight, thus lower than those observed by light scattering.

The obtained data indicated that, the reaction pattern seems complex and cannot be related to degradation of starch molecules alone. The difference between the results for gamma and EB irradiation could be referred to the differences in irradiation mode (continuous vs. pulsed), dose rate, and also
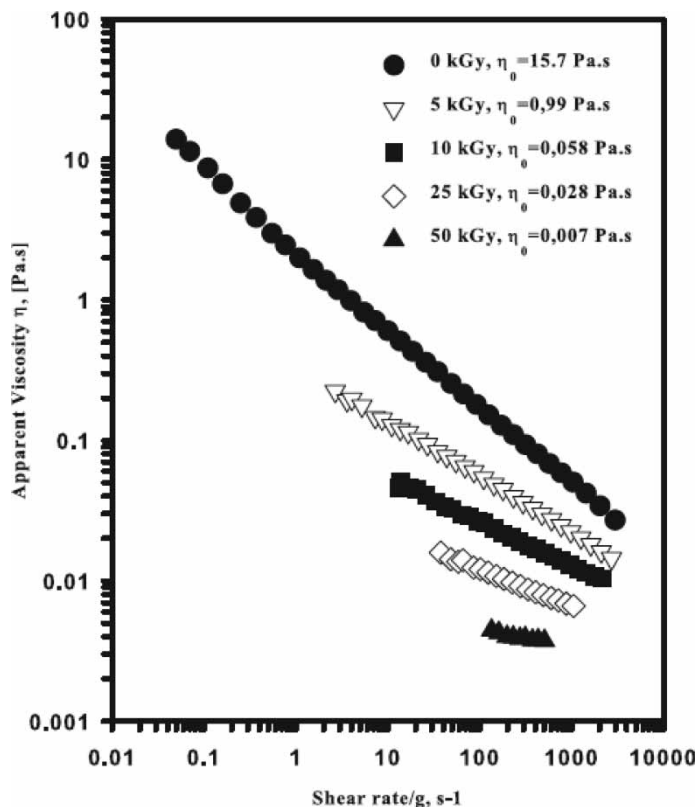
Fig. 5. Effect of shear rates on the apparent viscosity of starch irradiated as solid by electron beam starch concentration; 50 g L^{-1} in aqueous solution containing $5 \times 10^{-2} \text{ mol dm}^{-3}$ $NaClO_4$, dose rate; 5.10^2 kGy/h.

Fig. 6. Viscosity-average molecular weight of gamma and electron beam irradiated starch in the form of solid powder as a function of total absorbed dose. Mark-Houwink Parameters: $K = 1.44 \times 10^{-5} \text{ cm}^{-3} \text{ g}^{-1}$, a = 0.93, Temperature; 25°C, Starch concentration; 5 g L^{-1} in aqueous solution containing $5 \times 10^{-2} \text{ mol dm}^{-3}$ $NaClO_4$, EB dose rate; 5×10^2 kGy/h, gamma dose rate; 3.2 kGy/h.

difference in the degree to which oxygen interferes in both cases.

Figure 8 shows the effect of total absorbed dose on the apparent viscosity of starch irradiated with gamma and electron beam. It is clear that the electron beam affect on the apparent viscosity of starch is greater than that of gamma irradiation in the early stage of irradiation ~ 5 kGy. These results agreed with that previously reported (28−30). I was found that rheological properties of starch dispersions were dependent on the dispersed phase (granules), the continuous phase (amylose/amylopectin ratio) and the interaction between phases.

3.4   Influence of Irradiation Atmosphere on Corn Starch Degradation

Degradation and crosslinking of polymers are highly affected by the atmosphere of irradiation. Figure 9 shows the effect of absorbed dose in oxygen and argon atmosphere on the viscosity-average molecular weight (M_v) of corn starch determined by intrinsic viscosity. It was observed that, there is a significant decrease in M_v for samples irradiated in Ar-atmosphere, although, the degradation of starch in the oxygen-saturated solution was found to be slight protected.
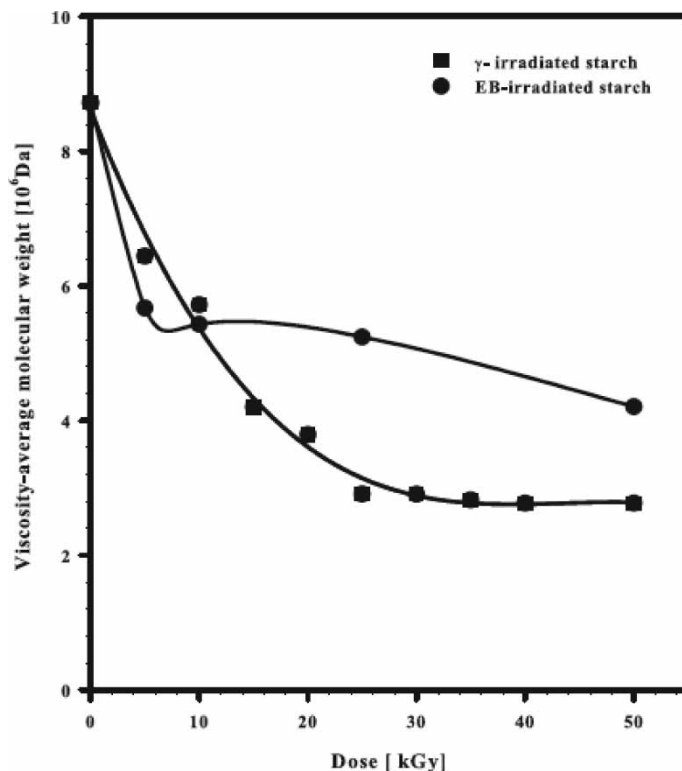
Such protection may be due to the formation of polar carbonyl groups in the presence of oxygen.

von Sonntag (31) reported that the oxidation reactions may lead to the formation of carbonyl groups of more hydrophobic properties. Thus aggregations occur in the radiolysis of disaccharides in deoxygenated aqueous solutions and it found that, scission of 1−4 glycosidic bonds is caused by rearrangement of radicals localized on C_1, C_4 and C_5 carbon atoms. Although fragmentation in the presence of oxygen can be described as the C1, C_4 and C_5 radicals are transformed into the corresponding peroxyl radicals, and these are less prone to degradation. Therefore, the mechanism of chain scission in starch may be rather complex.

3.5   Influence of Irradiation Atmosphere on the Radius of Gyration of Corn Starch

Table 1 shows the radius of gyration (nm) for gamma irradiated starch in O_2 and Ar-atmosphere at different irradiation doses. As it was observed from the data obtained, the radius of gyration decreases with increasing the irradiation dose. Generally, the R_g values for starch irradiated in oxygen-saturated solution were found to be greater
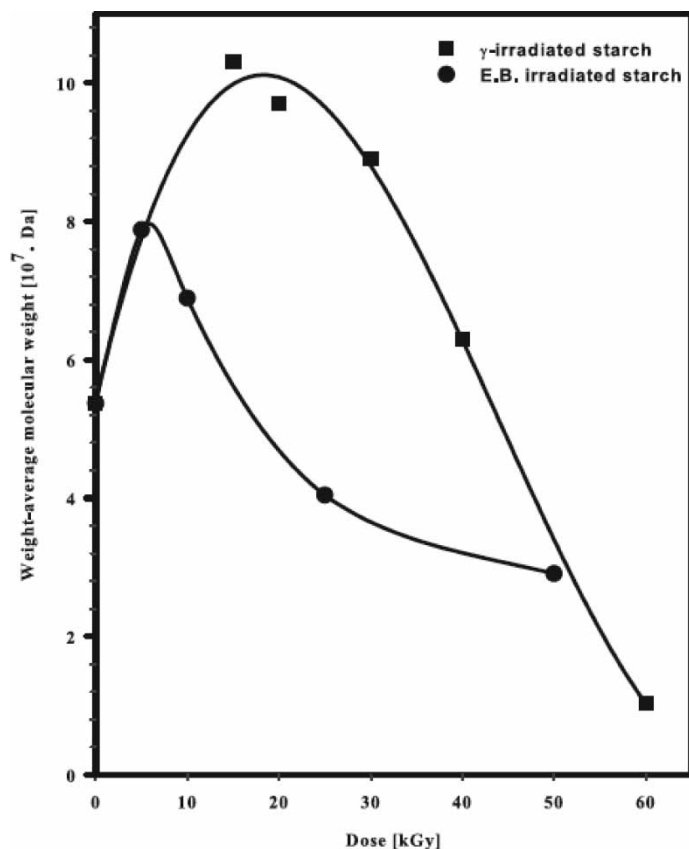
Fig. 7. Weight-average molecular weight of gamma and electron beam irradiated starch in the form of solid powder as a function of total absorbed dose, determined by multi-angle laser light scattering, Temperature; 25°C, Starch concentration; 5 g L^{-1} in aqueous solution containing 5×10^{-2} mol dm^{-3} NaClO$_4$, EB dose rate; 5×10^2 kGy/h, gamma dose rate; 3.2 kGy/h.

Fig. 8. Effect of absorbed dose on the viscosity of starch irradiated as a solid powder. Viscosity measurements were at starch concentration 50 g L^{-1} in aqueous solution containing 5×10^{-2} mol dm^{-3} NaClO$_4$, temperature; 25°C, EB dose rate; 0.141 kGy/h, Gamma dose rate; 3.2 kGy/h. Inside is the same plot but the initial stage of irradiation is magnifier.

than that of argon-saturated solution. According to the values of R$_g$ there is kind of protection for the whole molecule from degradation when it is irradiated in O$_2$. In some cases, oxygen may even exert a mild protective effect that reduce the degradation yield, as has been observed in the case of radiation-induced degradation of chitosan in aqueous solution (32).

Table 2 shows the concentration of unchanged glucose units for gamma irradiated corn starch, which was determined according to the *Anthrone method*. The decreasing in the glucose unit concentration reveals that, chemical changes were occurred in the starch molecules.

Figure 10 pronounces evolution of absorption spectra unirradiated and gamma irradiated starch at weavelength 265 nm. It can be seen that the absorbance of irradiated samples in O$_2$ atmosphere is higher than that irradiated in Ar-atmosphere. However, such absorption band is absent in the unirradiated starch, i.e., in the typical range for carbonyl groups absorption. Figure 11 shows the dose dependencies of absorbance at 265 nm wavelength. It is obvious that increasing efficiency of these changes is most pronounced
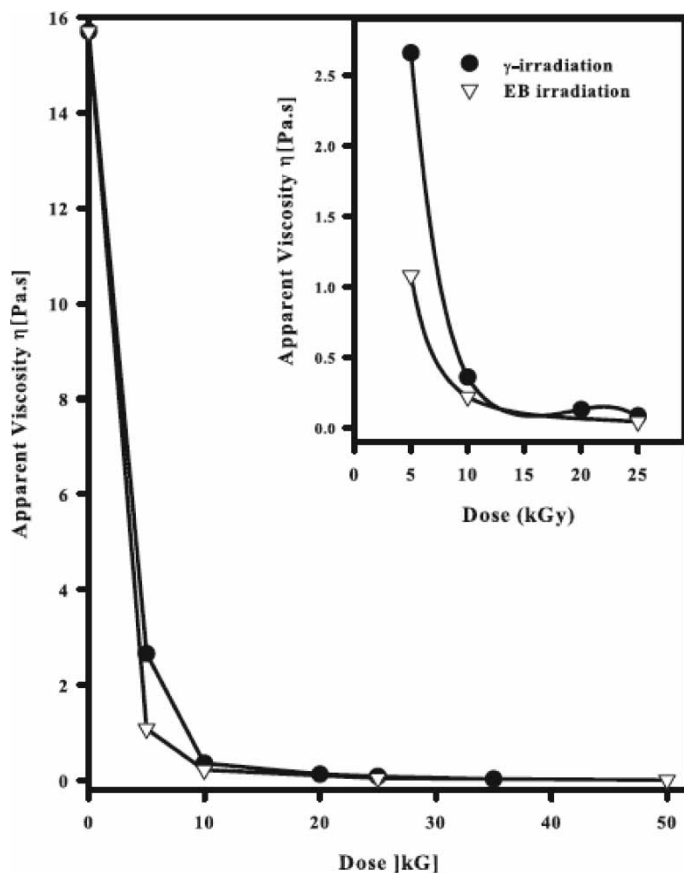
for samples irradiated in oxygen atmosphere. For oxygen-saturated solutions, the initial increase in the absorbance is due to increase in solution turbidity due to aggregation, since stronger aggregation in the presence of oxygen could be. A similar increase in absorbance at 265 nm was previously observed (33).

3.6 Determination of Changes in Weight Average Molar Weight

Figure 12 represent the Zimm plot for corn starch in 0.05 M NaClO$_4$. The extrapolation to zero angle yields the weight average molar weight M$_w \sim (4.4 \times 10^7)$ g mol^{-1}. The extrapolation to zero concentration gives a similar value M$_w \sim (4.4 \times 10^7)$ g mol^{-1} and the radius of gyration R$_g$ was about 199.3 nm. However, the absolute molecular weights of corn starch particles were above 10^8 g mol^{-1}, with radii of above 300 nm as determined from Berry plot with an error exceeding 20% (34). Therefore, M$_W$ and R$_g$
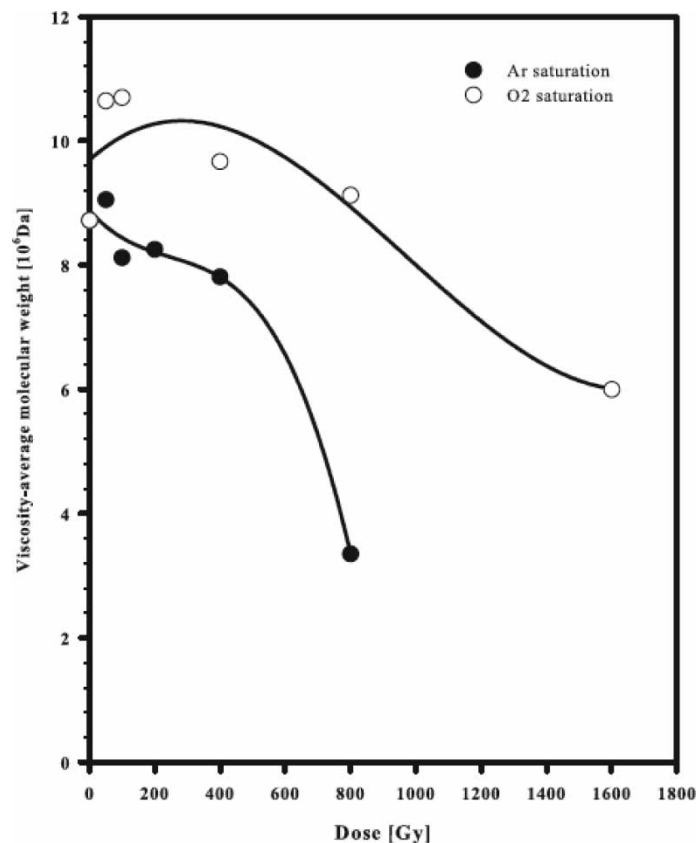
Fig. 9. Viscosity-average molecular weight of gamma irradiated starch in the form of solution as a function of absorbed dose in Ar or O_2 atmosphere. Temperature; 25°C, Mark–Houwink parameters: $K = 1.44 \times 10^{-5}$ cm^3 g^{-1}, a = 0.93, Dose rate; 90 Gy/h.

values within such regions should be understood as apparent values of molecular weight and radius of gyration.

To elucidate the effect of irradiation, corn starch samples were irradiated in air as a solid phase and in a diluted

Table 1. Radius of gyration of irradiated corn starch as a function of absorbed dose, determined by multi-angle laser light scattering irradiated as liquid in Ar or O_2 medium by gamma rays, Starch concentration 5 g L^{-1} in aqueous solution containing 5.10^{-2} mol dm^{-3} NaClO$_4$, Dose rate; 90 Gy/h

	Radius of Gyration (nm) of gamma irradiated starch	
Dose in Gy	Argon saturated	Oxygen saturated
0	199.3	199.3
50	216.5	102.3
100	112.3	142.4
200	135	101.4
400	121.9	115.3
800	104.4	152
1600	85.6	120.4

Table 2. The concentration of unchanged glucose units of irradiated corn starch as liquid in Ar or O_2 medium by gamma rays, as a function of absorbed dose

	Unchanged glucose concentration g/ml	
Dose in Gy	Argon saturated	Oxygen saturated
0	0.58	0.58
50	0.495	0.4
100	0.46	0.349
200	0.44	0.326
400	0.39	0.389
800	0.385	0.397
1600	0.315	0.397

aqueous solution (below 10%); Figure 13 shows the changes in the average molecular weight as a function of dose. It was found that in the initial stage of irradiation, the molecular weight increases, then it decreases with increasing the irradiation dose >20 kGy for both physical forms of starch. The initial increase in the molecular weight is due to the aggregation which is quite probable to occur upon
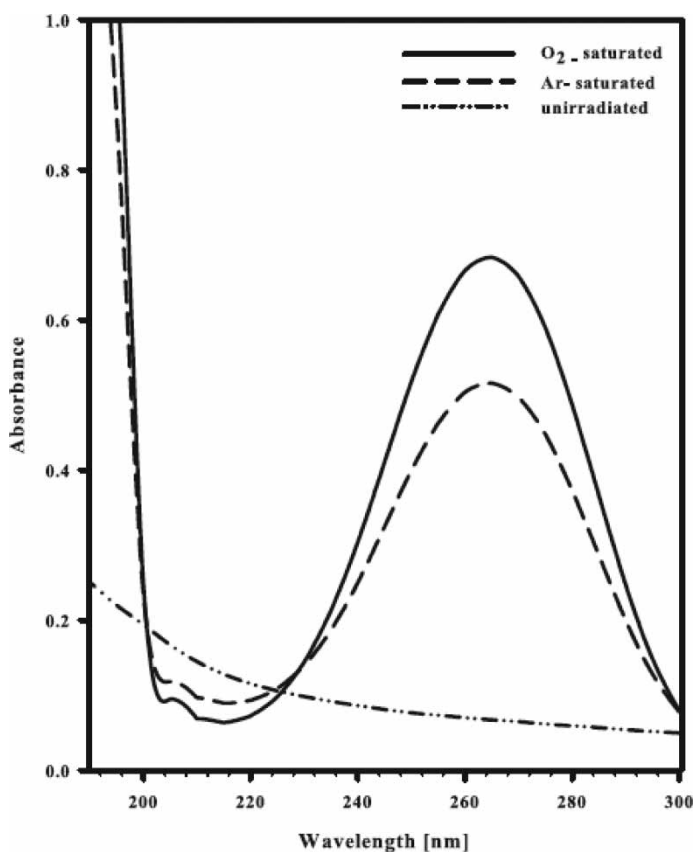

Fig. 10. Absorption spectra of unirradiated and gamma irradiated starch solution in Ar or O_2 atmosphere, the absorbed dose; 400 Gy, dose rate; 90 Gy/h.
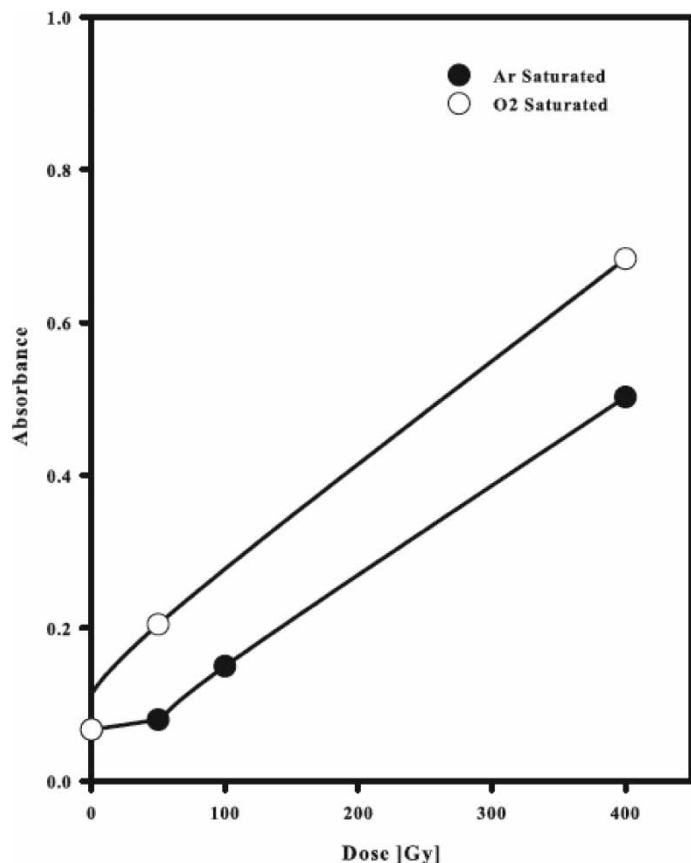
Fig. 11. Absorbance of gamma irradiated starch solution as a function of absorbed dose in Ar or O_2 atmosphere, at weave length; 265 nm. Dose rate; 90 Gy/h.

Fig. 12. Zimm plot for native corn starch in aqueous solution containing 5×10^{-2} mol dm^{-3} NaClO$_4$, The concentration of the scattering solutions are 0.1, 0.0778, 0.06363, 0.05, 0.039 g L^{-1}, respectively.

irradiation, since irradiation may lead to modification of chemical structure, for example to the formation of carbonyl groups. and this makes the polymer more hydrophobic and less water soluble. A further increase in absorbed dose lead to significant lowering in M_w as a result of starch degradation.

3.7   *Effect of Radiation on Radius of Gyration*

Because radius of gyration is related to the volume occupied by the chain-length and branching pattern of the molecule in a solution (35), the branch chain-length and branching pattern of the starch molecule are expected to affect the R_g of the starch in solution. Figure 14 represents the variation of radius of gyration with various doses. The R_g values of EB irradiated starch decreases as the irradiation dose increases. These results indicate that the size of the molecules decreased due to the degradation of starch components.

3.8   *FTIR of Irradiated Corn Starch*

The IR-spectrum gives very typical peaks for a number of special groups. As shown in Figure 15, starch is characterized
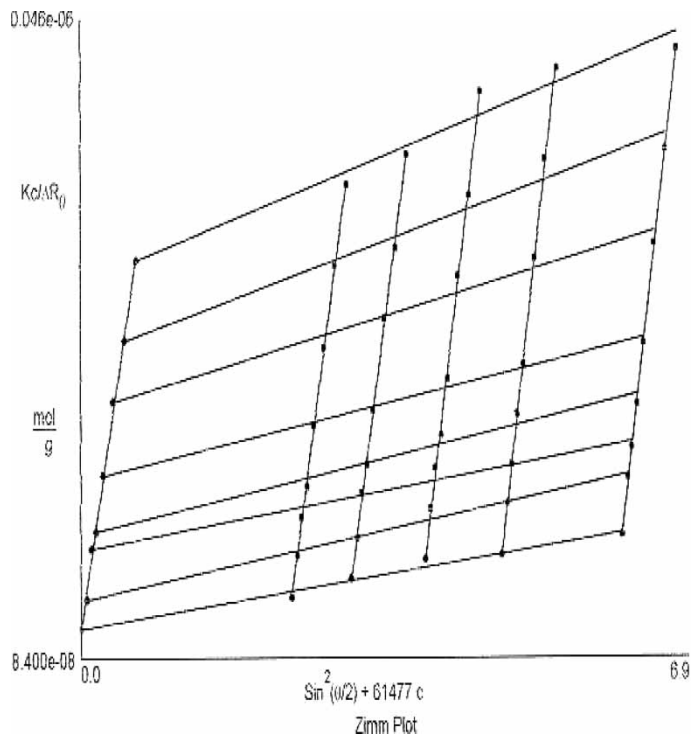
by two strong and broad absorption bands, OH stretching band occurring at 3900–3000 cm^{-1} and C-O-C stretching at 1250–900 cm-1, a minor C-H stretching band at 2930 cm^{-1}. These bands can both be used for qualitative starch analysis. The presence of OH group peak around 3400 cm^{-1}, is related to the presence of amylose and amylopectin (36). Irradiation affected the molecular weight distributions of amylose and amylopectin with the increase of amylopectin-like fractions (37). The breaking of the glycosidic bond was referred to be the most important change caused in polysaccharides by irradiation (38). The IR spectra of the electron beam irradiated samples shows that the OH stretching band centered around 3400 cm^{-1} is affected and increasing in the intensity of the characteristic peak at 1647 cm^{-1} was observed which is -O- tensile vibration band neighboring to H group, which can be related to carbonyl peaks. The increase in the intensity of this peak suggests that starch degraded by free radical reaction as previously proposed (39). All this confirms the strong effect of electron beam irradiation than the gamma one. Irradiation of starch by gamma rays involves two essential reactions which take place simultaneously: (a) oxidation of the starch hydroxyl to carbonyl groups and, (b) further oxidation of carbonyl groups to carboxyl groups. Nevertheless, decarboxylation, which may also occur concurrently with reactions (a) and (b), cannot be ruled out (40).
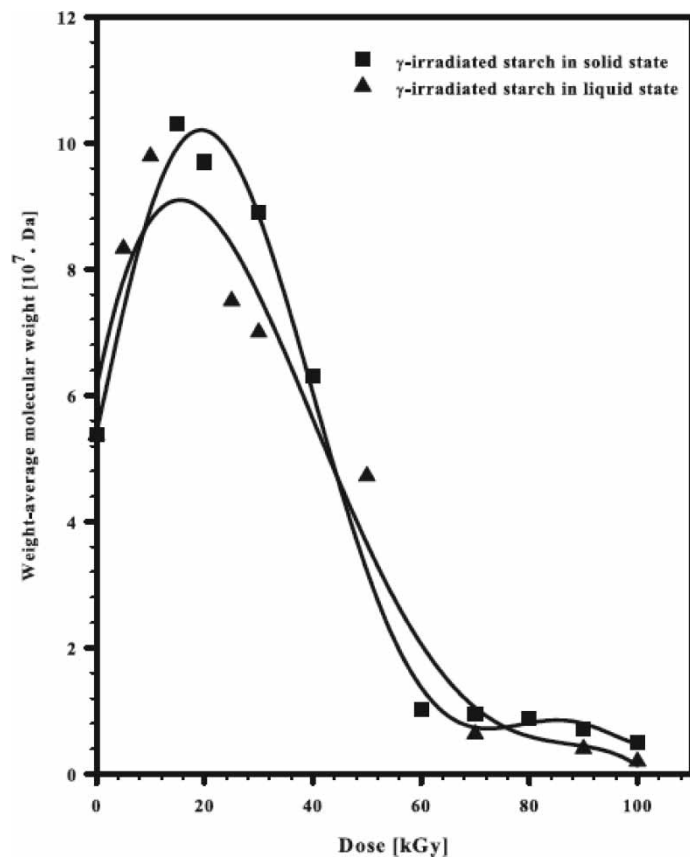
Fig. 13. Weight-average molecular weight of starch as a function of absorbed dose, determined by multi-angle laser light scattering, Starch irradiated as solid and as a solution, temperature: 25°C and dose rate; 3.2 kGy/h.

Fig. 14. Radius of gyration of electron beam irradiated starch as a function of absorbed dose, determined by multi-angle laser light scattering, Starch irradiated as solid powder, temperature: 25°C, dose rate; 5×10^2 KGy/h.

3.9 SEM Observation of Starch Granules

To elucidate the effect of electron beam and gamma irradiation on starch granules structure the morphology of unirradiated and irradiated corn starch granules with different doses were examined by scanning electron microscopy and shown in Figure 16. The shape of the starch granule was somewhat deformed by both gamma and electron beam. Irradiation and many of the granules were fragmented. Such observation represents further support for the view that ionizing radiation was capable of degrading starch into smaller fragments (41).

4 Conclusions

It can be concluded that, degradation of starch as a natural polymer is affected by the tools causing degradation (gamma rays or electron beam). The physical state (solid and liquid) of starch also affect its degree of degradation. The results suggest that irradiation in liquid form is more efficient if extensive degradation is to be desirable. The
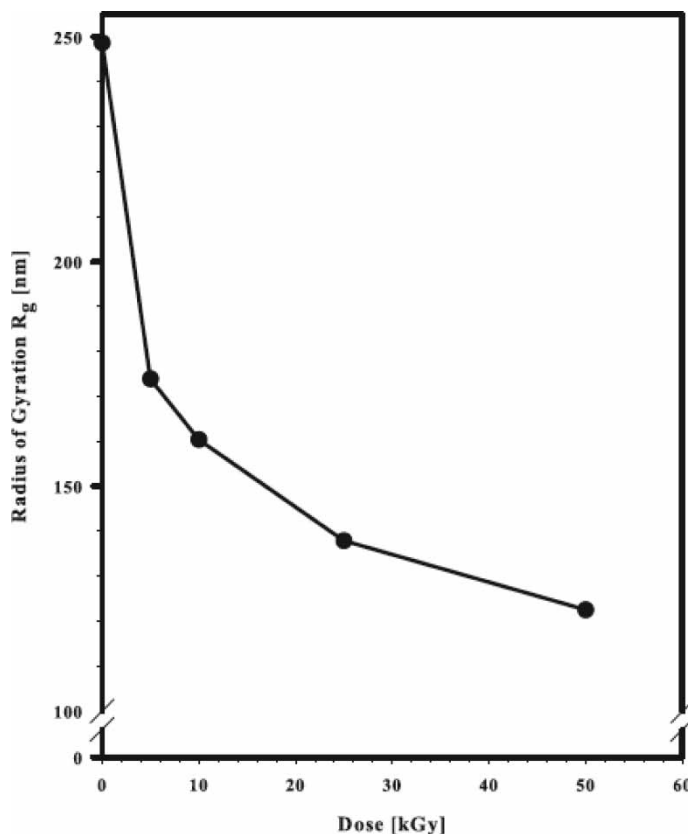
origin of differences between the results for gamma and EB irradiation could be referred to the difference in irradiation mode (continuous vs. pulsed) and associated difference in dose rate which affect the radical formation, and also the
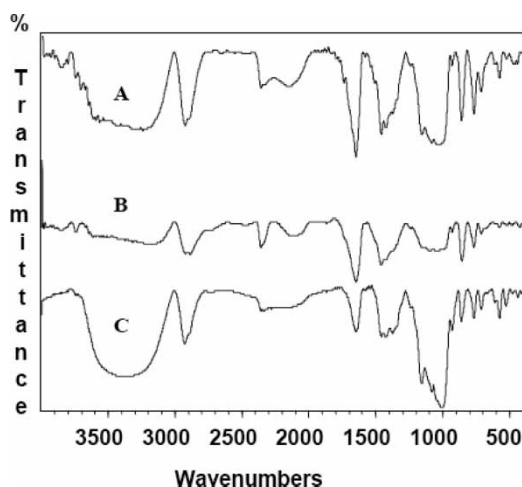

Fig. 15. The infrared spectra of corn starch. A: 50 kGy gamma irradiated; B: 50 kGy Electron beam irradiated corn starch; C: Unirradiated corn starch.
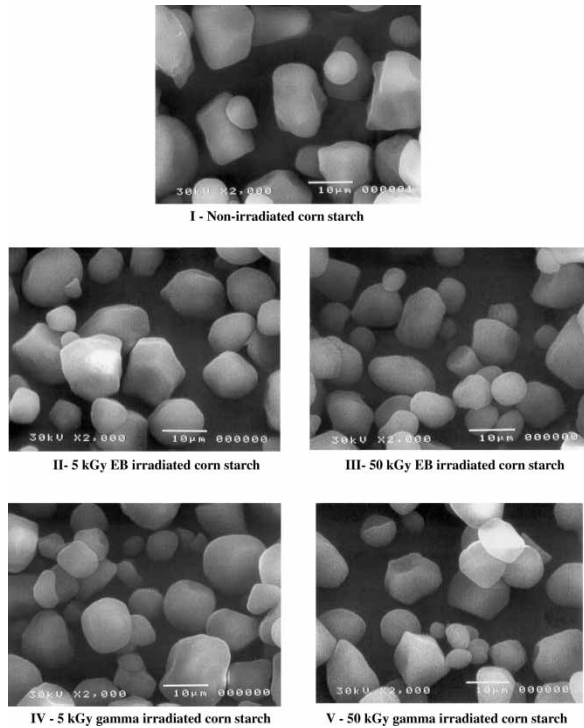
Fig. 16. Scanning electron microscopy of electron beam and gamma irradiated on corn starch granule.

penetration and degree to which oxygen interferes in both cases. According to the values of R_g for the samples irradiated in O_2 atmosphere and the increasing occurred in the absorbance of irradiated samples at weave length; 265 nm there is kind of protection for the whole molecule from degradation in the presence of oxygen.

5   Acknowledgements

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