

CRYSTALLINITY CHANGES OF ELECTRON-BEAM IRRADIATED ETHYLENE-VINYL ALCOHOL COPOLYMER (EVOH) AS A FUNCTION OF RADIATION DOSE

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ABSTRACT

The treatment with electron-beam radiation is a promising approach to the controllable modification of the properties of the polymeric materials, in order to adjust their properties. In recent years, electron-beam irradiation have been efficiently applied in the flexible packaging industry to promote cross-linking and scission of the polymeric chains in order to improve material mechanical properties. On the other hand, ionizing irradiation can also affect the polymeric materials itself leading to a production of free radicals. These free radicals can in turn lead to degradation and or cross-linking phenomena. In the present work the changes in thermal properties of electron-beam irradiated ethylene–vinyl alcohol copolymer (EVOH) resin were investigated. The EVOH resin was irradiated up to 500 kGy using a 1.5 MeV electron beam accelerator, at room temperature in presence of air. The EVOH samples irradiated from 300 kGy presented increases in melting temperature, except for 350 kGy. The changes in properties of the EVOH resin after irradiation were evaluated by differential scanning calorimetry (DSC) and X-Rays Diffraction (XRD). The correlation between the properties of EVOH non-irradiated and irradiated EVOH samples were discussed. The XRD results showed a slight shift of diffraction peaks, as well as an increase of width, DSC results also showed differences on crystallinity degree, for irradiated EVOH samples, which suggests that a decrease or an increase in degree crystallinity of EVOH will depends on radiation dose applied. These results are very important because shows a slight decrease in crystallinity of irradiated EVOH, a decrease in the crystallinity degree usually is related with an increase of the amorphous phase due to, probably, the predominance of molecular chain cross-linking of EVOH over the molecular chain scission and degradation process, caused by ionizing radiation, and a consequent improvement of their properties, such as thermal, mechanical, barrier and others.

1. INTRODUCTION

The constant search for superior properties in flexible packaging materials in order to be more competitive in this field made the use of ionizing radiation an efficient tool for controlled modification of chemical, mechanical, thermal and barrier packaging of polymeric materials, adding value and increasing the possibilities of application of flexible packaging. When applied to polymers, ionizing radiation can cause degradation (which is the breakdown of the main polymer chain) and crosslinking (chemical bonds between polymer molecules). Such reactions are competing and the predominance of one over the other depends on the chemical structure of the polymer, the process conditions of irradiation and other factors specific to the polymeric material, such as its processing history, degree of crystallinity and additives, among others[1-3].

The ethylene–vinyl alcohol copolymer is used as a barrier layer in packaging products that require high gas barrier. This higher barrier to gas is the most important property of the

EVOH, but also has other important properties such as resistance to permeation of oils, fats and organic solvents, good mechanical strength, elasticity and abrasion resistance. The EVOH has a great versatility allowing processing to be applied to packages that include flexible and rigid structures, being considered for packaging applications such as ketchup, barbecue sauce, mayonnaise, meat and other foods, packaging for solvents and other chemicals, and even tanks gasoline. However EVOH is very hygroscopic and in conditions of high humidity this polymer has a loss of its high barrier property [4-10].

The use of ionizing radiation on polymers is one of the biggest industrial applications of radiation, since the changes caused by irradiation in polymeric materials can lead to gains of certain properties; expand their scope and aggregate value to final product [11, 12]. In general, irradiation of polymers causes two simultaneous and concurrent processes, the cross-linking and degradation. These reactions are concurrent and the predominance of one or another depends on process conditions and the polymer itself, that is, type of radiation, the presence of oxygen, additives, degree of crystallinity and homogeneity of the absorber, among other [3, 11].

It is well known that physical, mechanical and barrier property of a crystalline polymer depends on the crystalline structure and degree of crystallinity [13]. For the evaluation of the crystalline and melting behavior of EVOH, in this paper, it was used X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The XRD analysis was used in order to estimate the crystalline fraction of EVOH and also the crystallite size that is a comparative parameter to evaluate the crystallinity of a material. The DSC analysis was used to determine the crystallinity percentage as well the melting temperature of EVOH. These both techniques were chosen in order to compare the results of crystallinity obtained.

The study of the effect of ionizing radiation on the EVOH resin, especially in its crystalline properties, which are linked to their gas barrier, will lead to obtaining knowledge that could result in improving the applicability of this resin in the packaging industry.

2. MATERIAL AND METHODS

2.1. Material

The material used in this study was the ethylene-vinyl alcohol copolymer (EVOH) resin containing 38 mol% ethylene (commercial grade by EVAL Company of America).

2.2. Electron-beam irradiation

EVOH samples were irradiated up to 500 kGy using a 1.5 MeV electrostatic accelerator (Dynamitron II, Radiation Dynamics Inc., 1.5 MeV energy, 25 mA current and 37.5 kW power), at room temperature, in air, dose rate 22.4 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters "CTA-FTR-125" from Fuji Photo Film Co. Ltd.

2.3. Differential scanning calorimetry (DSC)

The differential scanning Calorimetry (DSC) analyses were carried out using a DSC 50 (Shimadzu, Japan). DSC analyses of the materials were performed on three weighed samples with 4.0 ± 0.5 mg of the irradiated and non-irradiated materials. Samples were heated from room temperature to 300 °C, at a heating rate of 5 °C/min (in a nitrogen atmosphere). It was used the first heating to obtain the enthalpy.

Crystallinity was calculated from melting peak areas [14]. The percentage of crystallinity (X_c) was calculated using the relationship:

$$X_c = \frac{\Delta H_m}{\Delta H^0_m} \times 100 \quad (1)$$

Where: ΔH_m is the measured melting enthalpy of the sample - ΔH^0_m is initial melting enthalpy of the sample, for this work it was used as the initial melting enthalpy of the EVOH sample assuming 100 % crystallinity, 169.2 J/g for EVOH 38 % [15].

2.4. X-rays diffraction (XRD)

X-ray diffraction was carried out on a diffractometer Rigaku Denki Co. Ltd., Multiflex model with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 20 mA, with 2θ varying between 2° to 50° . Each diffraction pattern was normalized to make it possible the samples comparison from results obtained by using different counting times. For this analysis it was prepared samples with a plane surface by heating the EVOH to its melting temperature in order to enable this analysis (only after this process the samples were irradiated for XRD).

The crystalline fraction (%C) was determined using the equation 2 [16-19]:

$$\%C = \frac{I_c}{(I_c + KI_a)} \times 100 \quad (2)$$

Where %C is the crystalline fraction; I_c is the result of integration of the diffraction peak; I_a is the result of integration of amorphous halo; and k is a proportionality constant (for this work it was considered the Scherrer constant that is 0.94).

The crystallite size ($D_{(hkl)}$), was calculated following the equation 3 [2, 20, 21]:

$$D_{(hkl)} = \frac{k \lambda}{\beta \cos \theta} \quad (3)$$

Where k is the Scherrer constant, which depends upon lattice direction and crystallite morphology (0.94 is used in this study), λ is the wavelength of the $\text{Cu-K}\alpha$ ray, 2θ is the

diffraction angle of the peak, β is the FWHM (full-width at half-maximum height) given in radians and $D(hkl)$ the crystallite size that is obtained in Å.

3. RESULTS AND DISCUSSION

3.1. Differential scanning calorimetry (DSC)

The results of the DSC analysis for values of melting enthalpy (ΔH_m) and melting temperature (T_m) of the materials studied are given in Table 1. The crystallinity percentage (X_c) results is also given in Table 1. The results given in this Table represent the average values calculated from data obtained in analysis.

The results of melting temperature (T_m) showed that there were significant increases ($p < 0.05$) up to 5.6 % for irradiated EVOH up to 300 kGy when compared with the non-irradiated sample whereas for EVOH samples at 350 kGy where observed a slight decrease of 5.0 %. The results of ΔH_m showed slight differences depending on the radiation dose applied. Concerning the crystallinity percentage (X_c) results may be seen an increase of ca. 9.0 % for irradiated EVOH at 350 kGy and around 4.0 % at 450 kGy, when compared with non-irradiated samples. These results are very important because an increase in crystallinity can mean a gain in barrier properties and consequently, a reduction of their water absorption rate at high relative humidity conditions. An increase in crystallinity reduces the mobility of the amorphous chains leading to more efficient molecular orientation and to significant fall in permeation rates, since a rise in molecular organization makes the diffusivity of the liquid or gas more difficult. Considering that there is a direct influence between the EVOH water absorption rate, in their permeability, thermal and mechanical properties [22], these results can contribute to a better thermal and mechanical response of the materials at high relative humidity conditions compared to non-irradiated EVOH.

Table 1. Melting enthalpy, melting temperature and crystallinity percentage as a function of electron-beam radiation dose.

	DOSE (kGy)	ΔH_m^a (J/g)	X_c^b (%)	T_m^c (°C)
EVOH	0	58.45	34.54	156.30
	50	58.09	34.33	162.66
	100	54.53	32.23	156.04
	150	54.99	32.50	155.31
	200	53.29	31.50	155.31
	250	59.24	35.01	150.60
	300	53.86	31.83	163.08
	350	63.50	37.53	148.67
	400	59.80	35.34	163.25
	450	60.96	36.03	161.24
	500	58.78	34.74	165.03

a. Melting enthalpy; b. crystallinity percentage; c. melting temperature.

3.2. X-rays diffraction (XRD)

X-ray diffractograms of non-irradiated and irradiated EVOH are presented in Fig. 1.

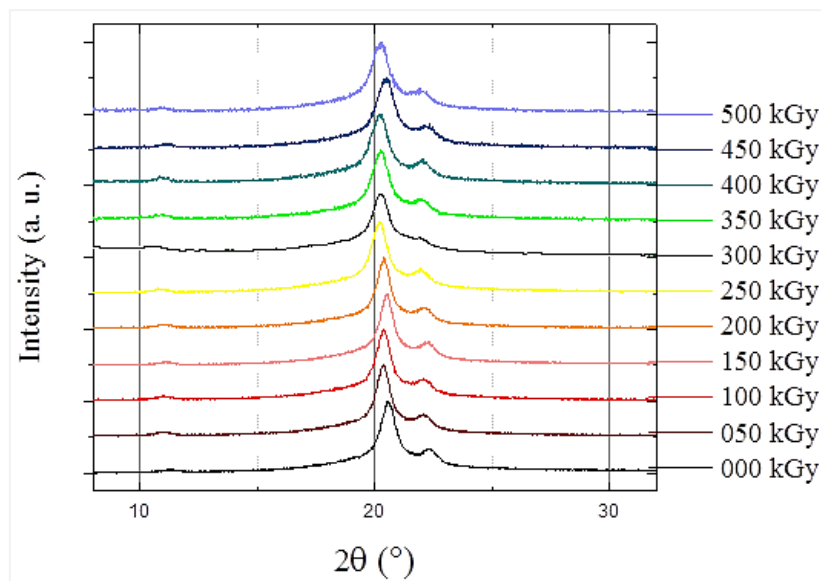


Figure 1. XRD normalized patterns of irradiated and non-irradiated EVOH.

As it can be seen there are two main peaks in 2θ , 20.54 (101) and 22.30 (200) and there were observed a slight shift of diffraction peaks, as well as an increase of width, for irradiated EVOH samples, these changes in the diffraction peak represent that there was a change in crystallinity degree. For EVOH, at the conditions of this work a decrease or an increase of crystallinity will depends on radiation dose applied, as it can be observed in Fig. 2, that present the results for the crystalline fraction (%) calculated by XRD results [13].

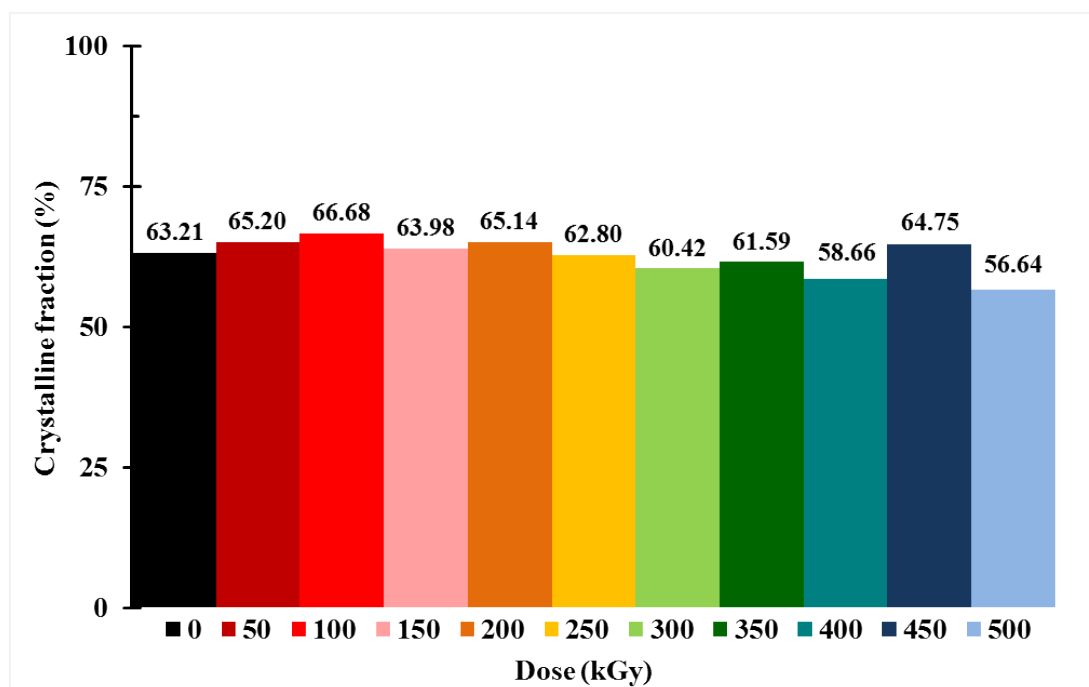


Figure 2. Crystalline fraction (%) calculated with the results of the XRD normalized patterns of irradiated and non-irradiated EVOH.

Comparing the results of crystallinity percentage (%) obtained by DSC analysis (Table 1) with the results of crystalline fraction (%) presented in the Fig. 2, it is noted that there were divergent results between the both analyses, which may be due to process to obtain the samples for the X-Rays diffraction analysis. The divergences observed can be explained by the intrinsic differences of each method used in the crystallinity calculus. The endothermic peaks (DSC) include many types of crystal, not only the biggest (more ordered) but also the smallest (less ordered). In XRD case the crystalline fraction calculus is made by the main peak [21, 23]. However these results showed that the use of electron-beam radiation for EVOH may cause changes in it crystallinity.

The results of calculated β (FWHM) and crystallite size ($D_{(hkl)}$) are presented in Table 2. As can be observed the results, for doses up to 350 kGy, of β (FWHM) showed an increase of the width of the diffraction peak that is inversely proportional to crystallite size. These results are important once a decrease on crystallite size may represent also a decrease in the molecular weight and crystallinity [19]. It means that the cross-linking takes place on irradiation, which

modifies the molecular structure and hinders the growth of crystal. Thus, the crystallinity decreases as suggests the predominant tendency of slight decreases of the crystallinity shown in Table 1 and Fig. 2.

Table 2. Calculated full-width at half-maximum height and crystallite size of non-irradiated and irradiated EVOH

	DOSE (kGy)	β^a (2θ)	$D_{(hkl)}^b$ (ηm)
EVOH	0	0.92	28.33
	50	0.87	29.96
	100	0.89	29.29
	150	0.83	31.41
	200	0.83	31.41
	250	0.93	28.03
	300	0.93	28.03
	350	0.98	26.60
	400	1.01	25.81
	450	1.08	24.14
	500	1.09	23.91

a. β is the FWHM (full-width at half-maximum height); b. Crystallite size that is obtained in converted in ηm .

4. CONCLUSIONS

This work showed that the use of ionizing radiation could lead to increase of the degree crystallinity of the EVOH; however the changes observed in DSC and XRD analysis, in the conditions of this work, showed that there were slight differences in degree of crystallinity of EVOH depending on the radiation dose applied. However there was a predominant tendency of slight decreases of the crystallinity. These results are very important because a slight decrease of irradiated polymer crystallinity, in this particular case, of EVOH, usually is related with an increase of the amorphous phase due to, probably, the predominance of molecular chain cross-linking of EVOH over the molecular chain scission and degradation process and a consequent improvement of their properties, such as thermal, mechanical barrier and others.

The results of melting temperature showed that there were significant increases up to 5.6 % for irradiated EVOH from 300 kGy compared with the non-irradiated sample, except for 350 kGy where it was observed a slight decrease of 5.0 %.

These results shows that electron-beam irradiation may be a potential method to the obtaining of EVOH resin with better barrier properties, lower water absorption, more stable thermal

and mechanical properties in high relative humidity conditions compared with non-irradiated resin.

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