Determination of the Crystallinity Index of Iron Polymethacrylate

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ABSTRACT: The crystalline fraction of γ-irradiated semicrystalline iron polymethacrylate was determined by X-ray diffraction analysis. In particular, the changes in the crystallinity index (CI) of the polymer as a function of the received dose (10–95 kGy) were studied and correlated with the parameters obtained by Mössbauer spectroscopy. We also analyzed the thermal degradation of the iron polymethacrylate in a sample with a maximum of crystallinity by employing the thermoanalytical techniques TGA and DSC. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 995–1002, 1999

Key words: crystallinity index; iron polymethacrylate; Mössbauer spectroscopy

INTRODUCTION

Crystalline polymers can show a preferential orientation of fibrous type, as well as the well-known crisscross type commonly called crosslinking.[1,2] When these types of polymers coexist in amorphous and crystalline structures, the substances are known as paracrystals. The amorphous fraction of a paracrystal contains some information concerning the crystalline order, because the amorphous fraction is an incoherent contribution due to the displacement of the scattered centers from their natural position in the arranged regular crystalline structure. To determine the amorphous fraction, several methods have been proposed.[3] In this work we studied the changes in the Crystalline Index during the γ-ray polymerization of the iron methacrylate, as well as the thermal degradation of the iron polymethacrylate (FePMA) in a sample where its crystallinity is maximum. The FePMA and other metal polymethacrylates have been briefly analyzed by Sarma et al. and Zulfiqar et al.;[4−6] herein we also present the determination of the maximum crystallinity that this semicrystalline polymer could acquire.

EXPERIMENTAL

Monomer Synthesis of Iron Methacrylate (FeMA)

Iron methacrylate was obtained by reacting equimolecular amounts of $NaHCO_3$, methacrylic acid and $FeCl_3$ as follows: an aqueous solution of $NaHCO_3$ was treated with methacrylic acid, the mixture was stirred for 30 min, then the $FeCl_3$ was added and stirred for 1 more h at 40°C. Precipitation of iron methacrylate were separated out by filtration, washed, and dried under vacuum.

The complete formation of the iron methacrylate was confirmed by gravimetric and spectrophotometric analysis.

When methacrylic acid reacts with $NaHCO_3$, the sodium replaces the hydrogen atom of the COOH group, and carbonic acid is produced; after that, three sodium atoms are replaced by the iron of the $FeCl_3$. Thus, iron methacrylate is obtained
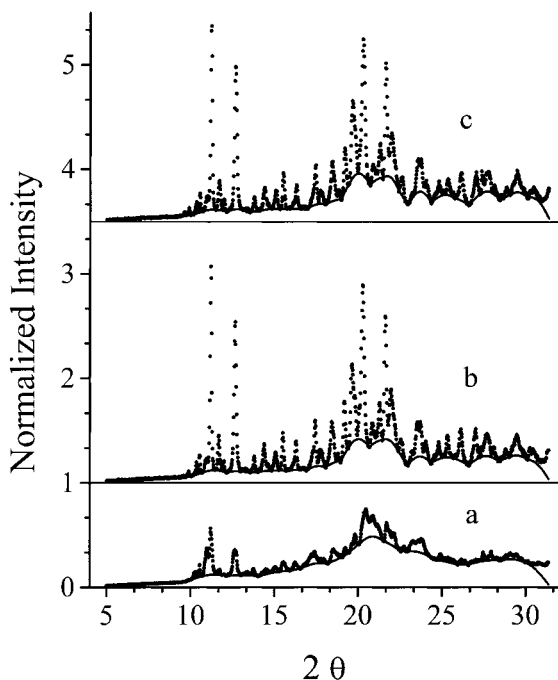
Figure 1 X-ray diffraction patterns of (a) monomer FeMA, which is more amorphous, (b) FePMA at 10 kGy, and (c) FePMA at 17 kGy. The continuous line indicates the amorphous fraction of the polymer, and the dotted one indicates the crystalline fraction.
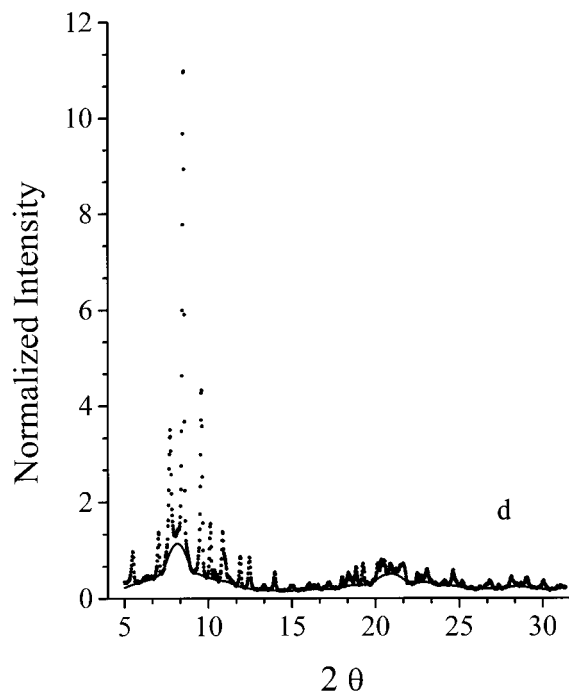

Figure 2 X-ray diffraction pattern of FePMA obtained at 25 kGy.

Determination of the Crystallinity Index of FePMA

To determine the CI of FePMA, samples containing 200 mg of the monomer were sealed in glass

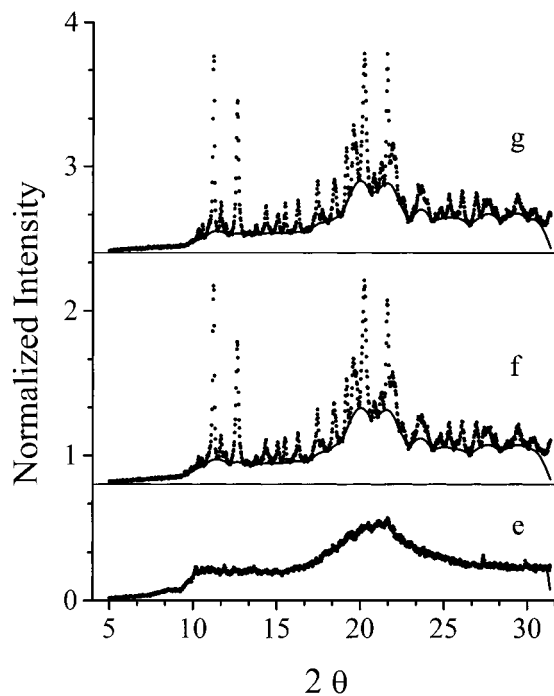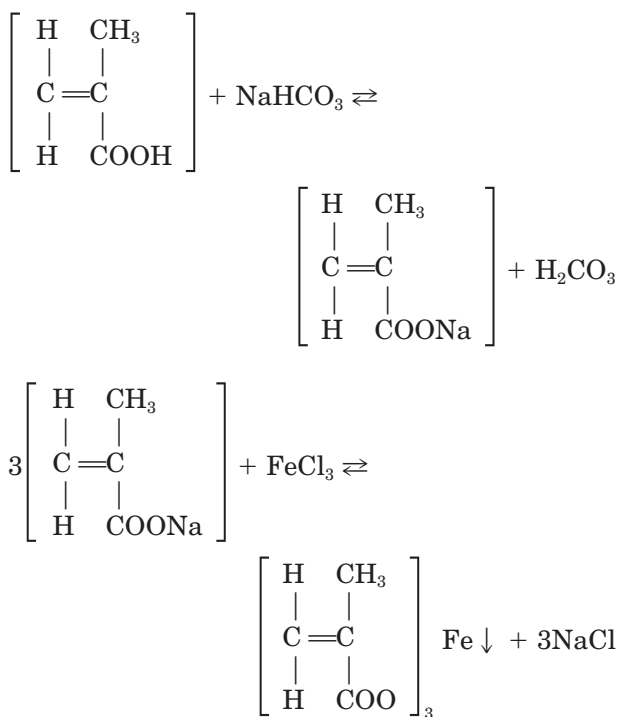in a solid form, whereas the formed NaCl remained in the solution.

$$
\begin{bmatrix} \text{H} & \text{CH}_3 \\ | & | \\ \text{C} = \text{C} \\ | & | \\ \text{H} & \text{COOH} \end{bmatrix} + \text{NaHCO}_3 \rightleftarrows
$$

$$
\begin{bmatrix} \text{H} & \text{CH}_3 \\ | & | \\ \text{C} = \text{C} \\ | & | \\ \text{H} & \text{COONa} \end{bmatrix} + \text{H}_2\text{CO}_3
$$

$$
3\begin{bmatrix} \text{H} & \text{CH}_3 \\ | & | \\ \text{C} = \text{C} \\ | & | \\ \text{H} & \text{COONa} \end{bmatrix} + \text{FeCl}_3 \rightleftarrows
$$

$$
\begin{bmatrix} \text{H} & \text{CH}_3 \\ | & | \\ \text{C} = \text{C} \\ | & | \\ \text{H} & \text{COO} \end{bmatrix}_3 \text{Fe} \downarrow + 3\text{NaCl}
$$

Figure 3 X-ray diffraction patterns of (e) FePMA at 40 kGy, at which it is completely amorphous, (f) FePMA at 50 kGy, and (g) FePMA at 65 kGy.
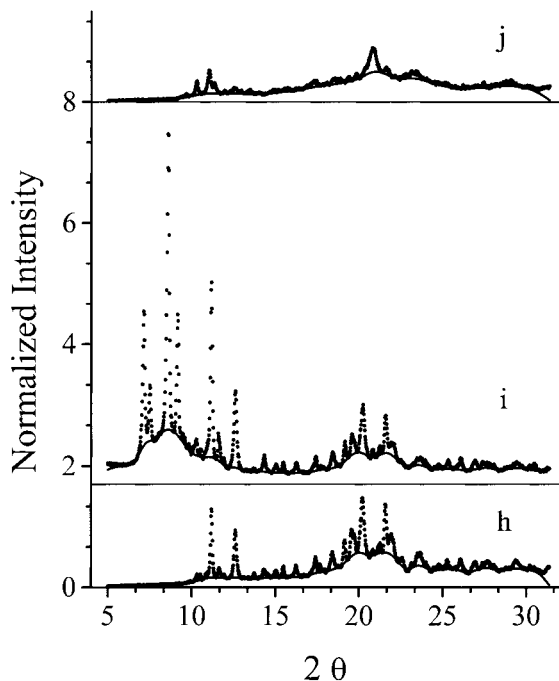
Figure 4 X-ray diffraction patterns of (h) FePMA at 70 kGy, (i) FePMA at 85 kGy, and (j) FePMA at 95 kGy, at which it is very similar to that obtained for the monomer.

Figure 5 TGA thermogram of FePMA at 25 kGy.

tubes under vacuum and irradiated at room temperature in a gamma irradiation unit gammacell-220, supplied with a ^{60}Co source. Doses of 10, 17, 25, 40, 50, 65, 70, 85, and 95 kGy to a dose rate of 0.5 kGy/h were applied.

X-rays spectra were obtained from each irradiated sample with a diffractometer θ-2θ Siemens D5000. Copper radiation was used with a diffracted beam monochromator tuned to ka radiation. The spectra were recorded at room temperature at a range of 5 to 31.38, with a step size of 0.02 (2θ). The counting time rate was 30 s/step. All the diffraction patterns were normalized to a NaCl standard pattern, and are shown in Figures 1, 2, 3, and 4. Ideally, the effects of the instrumental contribution on the patterns are the same for the amorphous and crystalline fractions in the paracryistal; for this reason any correction in this sense was made.
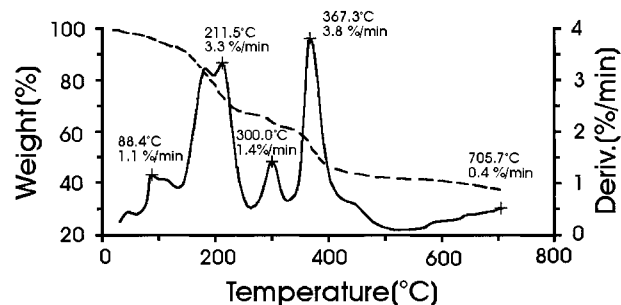
To determine the CI, the following expression[3] was used:

$$CI = \frac{IIUCS - BG}{IIUCS} 100 \qquad (1)$$

where IIUCS is the integrated intensity under the full spectrum, and BG is the background spectrum. The BG, i.e., the amorphous fraction, was calculated using a pass-low filter similar to the Burgess and Tervo method, which is used to calculate the background of gamma rays spectra.[7] The CI values calculated from the samples irradiated at different doses are given in Table I.

Two plateaus can be observed in this table, the first with approximately 10% more crystallinity than the second.

Thermal Degradation of the FePMA

To carry out the studies of thermal degradation we choose the polymer (FePMA) obtained at a dose of 2.5 kGy, which is located at the end of the first plateau (CI = 37%, Table I).

This sample was analyzed with a Thermogravimetric Analyzer (TGA-51 TA Instruments) and a Differential Scanning Calorimeter (DSC-10 TA Instruments) to determine its transition temperatures, and to decide at what temperatures the polymer will be heated to obtain its thermal degradation characterization.

The TGA analysis reveals a thermal stability until 80°C approximately; after that, the FePMA

Table I Crystallinity Index of Iron Polymethacrylate at Different γ-Doses

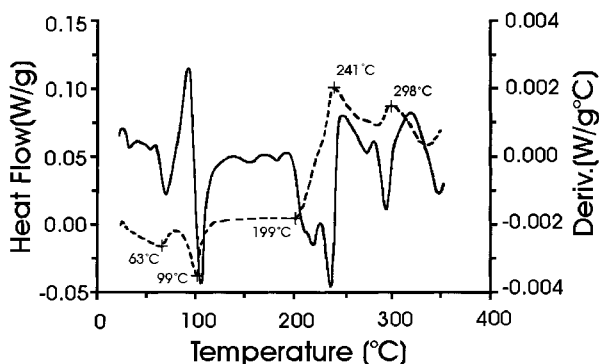| Dose (kGy)	0	10	17	25	40	50	65	70	85	95
CI (%)	18	39	37	37	4	27	27	25	30	18

Figure 6 DSC thermogram of FePMA at 25 kGy.

presents a weight lost, losing up to 30% at 260°C (Fig. 5). Four defined transition temperatures can be observed at 100, 205, 300, and 370°C, as it is also revealed from its derivative curve (same figure).

To corroborate these transition temperatures its DSC thermal curve was obtained. Transition temperatures around 100, 200, 240, and 280°C, are observed and also revealed from its thermal curve derivative in Figure 6. For completeness, Table II includes the transition temperatures of the monomer and the polymers obtained at 25 and 95 kGy.

From the comparison between TGA and DSC analysis, the following transition temperatures were chosen: 100, 200, 250, and 300°C. All the samples were heated for 6 h in the presence of air (open system); in addition, two samples were also sealed in glass tubes under vacuum (closed system) and heated at 100 and 200°C for the same period of time. These samples were analyzed by X-ray diffraction and Mössbauer spectroscopy.

Mössbauer Analysis

To analyze the changes in the Fe nuclei environment inside the monomer as well as in the irradiated and heated polymers, the Mössbauer spectra were obtained at room temperature with a ^{57}Co source imbided in a rhodium (Rh) matrix. In this way all the isomer shift (IS) reported values
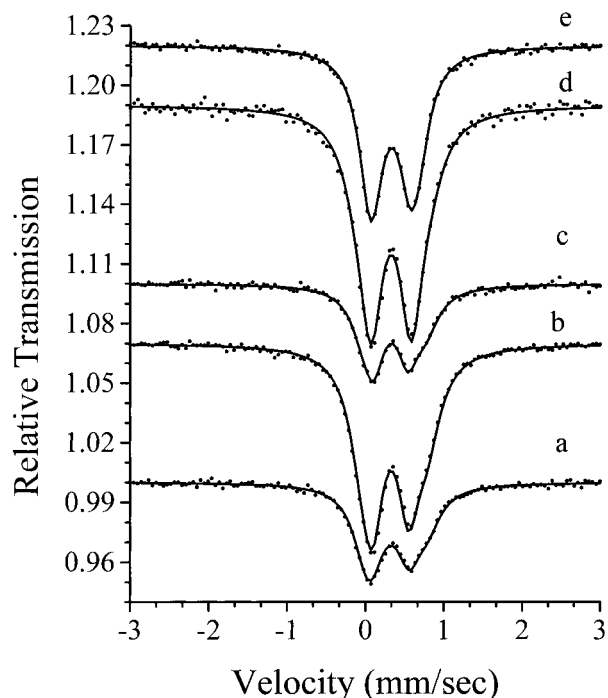

Figure 7 Mössbauer spectra of FeMA (a) and FePMA at different γ-doses (b) 10, (c) 25, (d) 40, and (e) 95 kGy.

are referred to a rhodium matrix. The spectra are shown in Figures 7, 8, and 9, and their characteristic parameters, isomer shift, and quadrupole splitting (QS) are given in Tables III, IV, V, and VI.

DISCUSSION AND RESULTS

The percentages of polymerization of the monomer (FeMA) after different periods of irradiation were different, showing an increase or decrease in its crystallinity concerning to the received dose. The maximum degree of polymerization obtained is according to Sarma et al.[5] at a 22 kGy dose, passing by a completely amorphous state at 40 kGy. In other words, the maximum interval of crystallinity corresponding to the first plateau is defined between 10 and 25 kGy, i.e., the maxi-

Table II   Transition Temperatures for FeMa and FePMA at 25 and 95 kGy

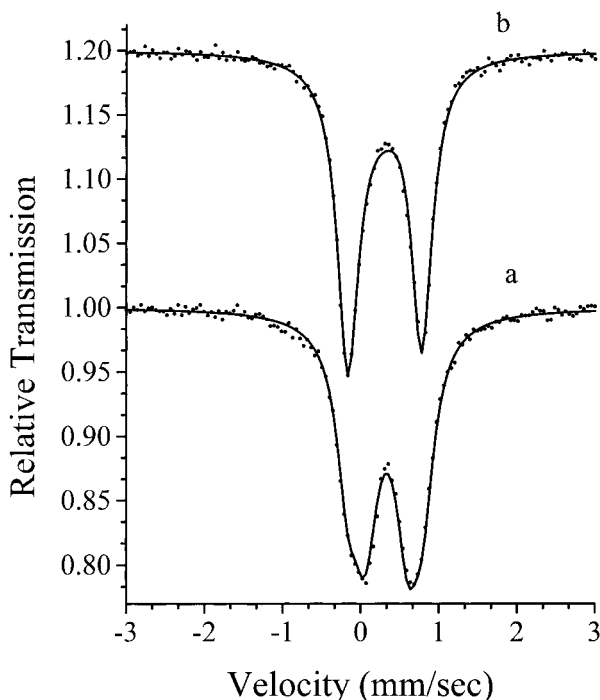| Dose (kGy)	Transition Temperatures °C				
0	98.1	205.5	240	288.5	367.3
25	88.5	200	235	300	367.3
95	84.6	200	240	292.3	365.4

Figure 8 Mössbauer spectra of (a) FePMA (25 kGy) heated at 100°C in an open system, and (b) FePMA (25 kGy) heated at 100°C in a closed system.

mum polymerization is within this interval (see Table I).

To our knowledge, the crystallinity of the FePMA has not been reported previously, but it is known that some polymers have a well-defined unit cell and crystallinity.[2] In this particular case, due the extended structure of the FeMA monomer, we think that the chain may propagate in the perpendicular direction, giving rise to a semi-crystalline polymer. Evidence of this can be observed in Figure 2, where the well-defined X-ray diffraction peaks indicate that the FePMA has a high crystallinity with few distortions in its crystalline lattice.

From the X-ray diffraction spectra (Figs. 1, 2, 3, and 4) it is observed that the radiation induces the formation of different reflection planes producing an increase or decrease in the interplane distances. An example could be seen in the spectra obtained from the samples irradiated at 10 and 17 kGy [Fig. 1(b) and (c)].

The X-ray pattern obtained from the heated polymer (closed system) at 100°C is different from that obtained from the polymer heated at the same temperature in an open system (Fig. 10). Furthermore, its CI value of 34.8 is 10% higher than in the open case. The observed differences in

CI values and planes for the closed and open systems are probably due to the additional pressure generated from the emanating gases in the closed system during the polymer heating. It is known that pressures higher than atmospheric induce a better ordering of the scattered centers. It must be mentioned that the open and heated polymer shows an CI of 12% smaller than the unheated one, and that the closed and heated polymer has a CI slightly smaller than the unheated one.

The asymmetric doublets showed in the Mössbauer spectra (Fig. 7), were first analyzed using two independent Lorentzians for its fitting. As a result, the percentage area of each line with respect to the total area of its respective spectrum, were $52 \pm 2\%$ and $48 \pm 2\%$. These results suggest that the spectra are formed by two symmetric doublets. However, when the spectra were reanalyzed using two doublets, the chi square was reduced by approximately 10%. The values of the recovered parameters in the fitting are shown in Tables III and IV. The recovered values of IS were the same from both doublets within the experimental error of the spectrometer, and the values of the QS parameter exhibit only small variations, confirming that the experimental spectrum
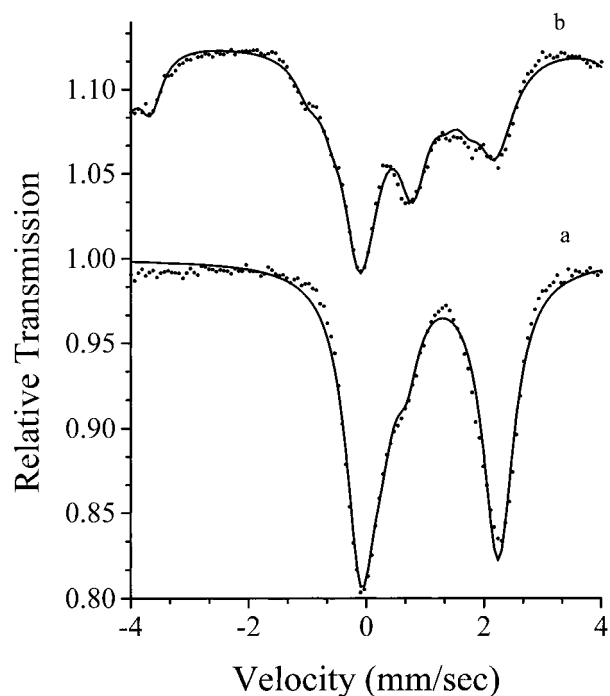

Figure 9 Mössbauer spectra of FePMA (25 kGy) heated at 200°C in an open system (a) and at 250°C in an open system (b).

Table III   Mössbauer Parameters of the Crystalline Spectra of FeMa and FePMA at Different γ-Doses

Dose (kGy)	0	10	17	25	40	50	65	70	85	95
Width mm/s	0.39	0.41	0.4	0.41	0.41	0.41	0.41	0.42	0.42	0.32
IS mm/s	0.39	0.37	0.37	0.38	0.35	0.36	0.36	0.36	0.36	0.38
QS mm/s	0.83	0.83	0.83	0.79	0.97	0.83	0.85	0.83	0.83	0.65
Area (%)	29	38	36	40	14	41	41	43	41	21

is formed by two doublets. Regarding these results, we can say that the analysis of the irradiated polymers by Mössbauer spectroscopy reveal two symmetrical doublets with an average (IS) of 0.37 mm/s, for the crystalline phase, and 0.39 mm/s for the amorphous one, both corresponding to Fe^{3+}.

Comparing the CI values showed in Table I with the area percentage values given in Table III, one can observe that some of these values are very similar, and that the difference among the other values are small; such values correspond to the crystalline fraction of the FePMA. To sum up, we can say that the doublet with a lesser contribution to the total spectrum corresponds to the crystalline polymer.

In this case, the Mössbauer spectroscopy is able to discern between the crystalline and amorphous phases that are present in the FePMA. This can be explained due to the fact that the Fe nuclei can be set in two different groups with a specific distribution of their electrons from the "d" shell for each one.

The polymer is amorphous at a 40 kGy dose, and it is possible that at this dose the polymer shows a maximum crosslinking because the Mössbauer effect presents its maximum absorption [Fig. 7(d)]. This assumption is based to the fact that this kind of polymers when irradiated preferentially undergo main-chain cleavage, giving rise macroradicals that generate a crosslinked structure.[8] However, it must be mentioned that when a polymer is subjected to ionizing radiation,

positive ions, free electrons, and excited molecules are formed in the polymer; additionally, reactions of these primary products leads to formation of a second generation of active intermediates like positive ions, negative ions, and free radicals. Reaction of primary and secondary intermediates introduces some permanent changes such as crosslinks, degradation, and saturation. These changes occur more frequently at higher doses.[9] We assumed that at doses over 40 kGy degradation and saturation effects are predominant. Typical reactions of irradiated polymers are reported by other authors elsewhere.[10,11]

The polymers (open and closed systems) heated at 100°C, show two Mössbauer doublets [Fig. 8(a) and (b)], with isomer shifts of 0.33 mm/s and 0.32 mm/s for the first ones, and 0.13 mm/s and 0.30 mm/s for the second (Table V), all of them corresponding to a Fe^{3+} in a high-spin state with a noncubic symmetry. Although both doublets did not show any change in the state of Fe^{3+} with respect to the unheated polymer, we found three different QS values (0.55, 0.97, or 0.94, and 0.36 mm/s) for the heated polymers and two for the unheated ones (0.44 and 0.83 mm/s).

The QS values suggest that there are three crystallography symmetry planes; the one with the highest QS value (approx. 0.97 mm/s) corresponds to the lowest symmetry.

The fractions of the amorphous and crystalline phases in the open system are 66 and 34%, respectively. According with the CI values determined by X-ray diffraction, their areas are differ-

Table IV   Mössbauer Parameters of the Amorphous Spectra of FeMA and FePMA at Different γ-Doses

Dose (kGy)	0	10	17	25	40	50	65	70	85	95
Width mm/s	0.4	0.35	0.36	0.33	0.38	0.33	0.33	0.34	0.34	0.37
IS mm/s	0.32	0.32	0.32	0.33	0.33	0.32	0.33	0.33	0.33	0.32
QS mm/s	0.48	0.46	0.46	0.44	0.52	0.43	0.43	0.44	0.45	0.51
Area (%)	71	62	64	60	86	60	59	57	59	79

Table V   Mössbauer Parameters of FePMA (25 kGy) Heated at 100 and 200°C in Open and Closed Systems

System	Open		Closed		Open		Closed	
	1 dob.	2 dob.	1 dob.	2 dob.	1 dob.	2 dob.	1 dob.	2 dob.
Temp. (°C)	100	100	100	100	200	200	200	200
Width mm/s	0.41	0.34	0.56	0.32	0.64	0.58	0.64	0.51
IS mm/s	0.33	0.32	0.13	0.30	1.03	0.47	1.07	0.48
QS mm/s	0.55	0.97	0.36	0.94	2.28	0.49	2.32	0.40
Area (%)	66	34	16	84	81	19	84	16

ent, with CI values of 76 and 24%, corresponding to the amorphous and crystalline fractions, respectively. It will be expected that the real CI value should be between 24 and 34%.

For the case of the closed sample, the calculated CI by Mössbauer spectroscopy was of 84%, which is higher than that calculated by X-ray diffraction (35%). This notorious difference is probably due to the contribution of the doublet to the total spectrum (IS = 0.30 and QS = 0.94 mm/s), as it is made from an amorphous fraction and the other crystalline. Besides, the doublet with parameters IS = 0.13 and QS = 0.36 mm/s is a small fraction (16%), and probably also contributes to the amorphous fraction that corresponds to the crosslinked material. However, none of the doublet's Mössbauer parameters coincide with the corresponding amorphous fraction in the closed heated polymer (IS = 0.33 and QS = 0.55 mm/s), as it is shown in Table V.

The open and closed polymers heated at 200°C exhibit the same Mössbauer spectrum [Fig. 9(a)]. The spectrum shows a large symmetric doublet corresponding to the phase transition to Fe^{+2},

**Table VI   Mössbauer Parameters of the Subspectra of FePMA (25 kGy) Heated at 250°C**

Subspectra	1[oa]	2[oa]	3[ob]	4[ob]
Width mm/s	0.98	0.21	0.66	0.82
IS mm/s	0.55	0.20	0.39	1.00
QS mm/s	0.01	0.04	0.89	2.32
Field T	46.2	49.3	—	—
Area (%)	54	6	20	20
Lines	6	6	2	2

[a] These values were obtained from the fitting of the spectra scanned in the range (−10, 10).
[b] These values were obtained from the fitting of the spectra scanned in the range (−4, 4).

and another small symmetric doublet associated with the amorphous phase corresponding to the previous phase of Fe^{+3}, as it is also shown in Table V. The change in spin is probably due to the decomposition of the FePMA and a subsequent donation of an electron to the Fe^{+3} for any free radical produced in the system. The resulting product is characteristic of Fe^{+2} with a high spin, which can be assigned to be $Fe(C_2O_4)$ in accordance with their average parameters, IS = 1.05 mm/s and QS = 2.3 mm/s.[12] In this case, the degraded polymer is completely amorphous.

Figure 9(b) shows the Mössbauer spectrum of the FePMA heated at 250°C, and its Mössbauer
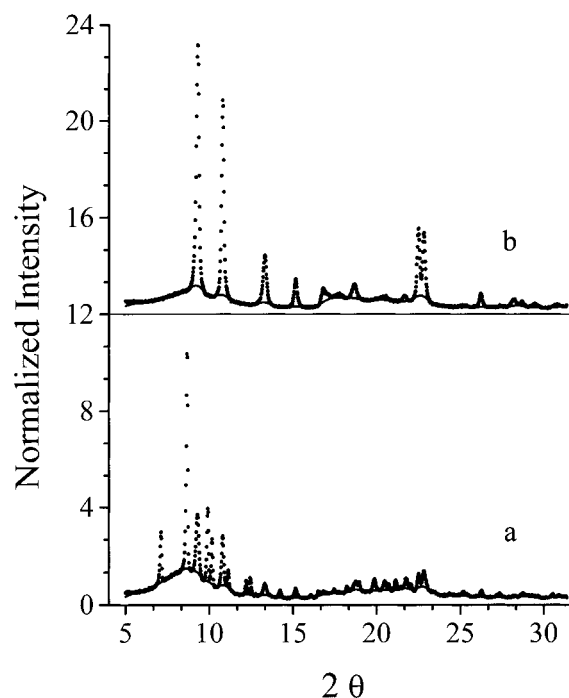
Figure 10   X-ray diffraction patterns of (a) FePMA (25 kGy) heated at 100°C in an open system, and (b) FePMA (25 kGy) heated at 100°C in a closed system.

parameters are given in Table VI. As can be observed, subspectra 1 and 2 correspond to magnetite (Fe_3O_4), which corroborate the thermal degradation of the polymer. Isomer shift (0.39 mm/s) and quadrupole splitting (0.89 mm/s) from subspectrum 3 correspond to a crystalline phase (see Table III). For the subspectrum 4, the values of IS and SQ are similar to those obtained at 200°C, (1.00 and 2.32 mm/s), corresponding to $Fe(C_2O_4)$.

At a temperature of 300°C, the polymer is completely degraded, showing the typical magnetic spectrum of Fe_3O_4. This double sextet corresponds to the presence of particles with sizes bigger than 160 Å, because the superparamagnetism peak is absent.

CONCLUSIONS

The semicrystalline polymer FePMA subject to different γ-ray doses presents notorious changes in its crystallinity index. These changes also depend on the pressure to which the polymers are subjected during their thermal degradation. The maximum CI value of FePMA corresponds to the maximum degree of polymerization at 25 kGy. Mössbauer spectroscopy and X-ray diffraction show that the unheated polymers have less than 50% of crystalline material.

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