CHAPTER FOUR
THE RESULTS

The present work is carried out by studying the effect of three anioxidents which are N-isopropyl-N'-phenyl-p-phenylene diamine (IPPD), phenyl B-naphthylamine (PBN), and N-(1, 3-dimethylbutyl)-N'-phenyl-p-phenylene diamine (6PPD) at 1 phr on improving the performance of NBR and EPDM seal materials. The studied antioxidants belong to P-phenylene diamines (PPD) group. Each formulation compound (was irradiated at different doses up to a maximum of 5MGy.

In the present work the testing was subdivided into comprehensive testing on linear materials in sheet form and molded O-ring seal form.

4.1 Cure Characteristics

The Oscillating Disk Rheometer (ODR) is used to measure the complete curing characteristics [32, 96] of the rubber compounds from uncured stock to a fully cured vulcanizates at a specified temperature (ASTM D-1646 and D-2084). Data of the cure characteristics from ODR for different PPDs antioxidants loaded the NBR and EPDM rubber compounds are shown in Table (4.1) and (4.2) respectively.

The minimum torque (M_L) is a measure of the extent of mastication, whereas the maximum torque (M_H) is an indication of the cross-linking density of the fully vulcanized rubber. It is obvious from the rheological data that the minimum and maximum torque (M_L and M_H, respectively) decrease for the NBR compounds (table 4.1) with addition of PPDs antioxidants materials. It is also clear that these different in the torque values may be due to the cross-linking density in the matrix of the rubber. While the minimum and maximum torque (M_L and M_H, respectively) increase for EPDM compounds (table 4.2) with the addition of PPDs antioxidants materials which mean there is an increasing in the crosslinking density. The scorch time (t_{s2}) is a measure of the time at which vulcanization of the mixes begins.

Tables 4.1 and 4.2 illustrate that NBR with 6PPD antioxidant (NC), and EPDM without antioxidants (EO) show better scorch safety. The optimum cure time (t_{c90}) is usually taken to mean the time for vulcanization of the rubber compound at a definite temperature to obtain optimum physical properties. Usually, the optimum cure is taken at time for 90% or 95% rise in recorded torque for a rheograph. The rise in torque is considered to be proportional to the rise in crosslink density, thus this represents 90% or 95% completion of the crosslinking reaction [(19)]. From the tables 4.1 and 4.2 it is clear that NC and EO have the highest values.

The cure rate index (CRI) is the measure of rate of vulcanization based on the difference between optimum vulcanization and the scorch time. It can be calculated from the relation:

$$\mathbf{CRI} = \frac{100}{T_{C90} - T_{S2}}$$

Too long cure times may cause reduced network stability and a reduction in properties of vulcanized rubber.

Table (4.1)

Vulcanization Parameters

Property	NO[1]	NA[2]	NB[3]	NC[4]
M_L (Lb in)[a]	1.3	1.15	1.05	1.04
M_H (Lb in)[b]	23.60	20.40	19.12	20.39
t_{s2} (min)[c]	1.77	1.31	1.47	2.61
t_{c90} (min)[d]	4.12	3.83	3.41	5.97
CRI (min^{-1})[e]	42.55	39.68	51.54	29.76

[1]NBR without antioxidants
[2]NBR with IPPD antioxidant
[3]NBR with PBN antioxidant
[4]NBR with 6PPD antioxidant
[a]Minimum Torque
[b] Maximum Torque
[c]Scorch Time.
[d] Time of 90%Cure
[e] Cure rate index

Table (4.2)

Vulcanization Parameters

Property	EO[1]	EA[2]	EB[3]	EC[4]
M_L (Lb in)[a]	1.96	2.10	2.27	2.30
M_H (Lb in)[b]	12.77	13.88	15.43	15.40
t_{s2} (min)[c]	4.51	3.66	3.87	3.81
t_{c90} (min)[d]	8.77	8.54	8.47	8.46
CRI (min^{-1})[e]	23.47	20.49	21.74	21.50

[1]EPDM without antioxidants
[2]EPDM with IPPD antioxidant
[3]EPDM with PBN antioxidant
[4]EPDM with 6PPD antioxidant
[a] Minimum Torque
[b] Maximum Torque
[c] Scorch Time.
[d] Time of 90%Cure
[e] Cure rate index

The results seemed to be dependent mainly on the antioxidant type in the rubber compound. In rheometer test, initially, there is a sudden increase in torque as the chamber is closed. Then, as the rubber is heated, its viscosity decreases, causing a decrease in torque. Eventually, the rubber compound begins to vulcanize and transform into elastic solid, and the torque rises. Molecular chain scission also may be occurring; however, an increasing torque indicates that crosslinking is increased. If chain scission and / or crosslinking breakage become dominant during prolonged heating, the torque passes through a maximum and then decreases, a phenomenon termed reversion.

4.2 Results of Linear Materials

4.2.1 Physical Properties

Determination of swelling ratio and crosslinking density of the radiation vulcanized NBR and EPDM rubbers are carried out in toluene at room temperature and the results are shown in figures 1- 4.

The effect of deterioration due to the prolonged exposures of□ γ-irradiation up to high doses on the swelling ratio values of the rubber samples NBR, EPDM in Toluene; is shown in Figures 1 and 2 respectively at room temperature.

In Fig. 4.1, NBR rubber compounds (NO, NA, NB and NC) show that generally the swelling ratio decreases with increasing γ-doses. However, the present results show that NBR without antioxidants (NO) have lowest value of swelling ratio while NBR with 6PPD antioxidant (NC) has the highest value. The other two studied rubber compounds: NBR with IPPD antioxidant (NA) and NBR with PBN antioxidant (NB) have values almost close together.

Fig. 4.2 shows the swelling ratio of the studied EPDM compounds decrease with increasing γ-doses. It can be observed that EPDM without antioxidants (EO) has the highest value of swelling ratio at zero radiation doses. In adding of the specified antioxidants, the swelling ratio value is going to be less than that EPDM rubber without antioxidants at zero radiation. The swelling ratio values decrease, for all studied EPDM compounds, with increasing gamma dose up to 1 MGy. While at high γ-doses, the swelling ratio values are not significantly changes for all studied EPDM compounds.

Fig. 4.3 shows the effect of gamma rays on the crosslinking density of NBR rubbers with PPDs antioxidants. To demonstrate the low dose effect up to 2MGy, a built in figure is drawn inside figure 4.3. It shows that the crosslinking values at no irradiation are almost with the same value order. Generally crosslinking density increases with increasing doses for low dose level part. At 2MGy, the highest crosslinking is recorded by NBR without antioxidant (NO) followed by NBR with IPPD antioxidant (NA). The lowest crosslinking density value is achieved by NBR with 6PPD antioxidant (NC) rubber compound. For both NO and NA have the same trend, they increase with increasing the dose up to 4MGy, for further increase, the irradiation doses the crosslinking density is suddenly decreased. NBR with PBN antioxidant (NB) sharply increases crosslinking density with increasing dose; while NC has the lowest crosslinking density at high doses.

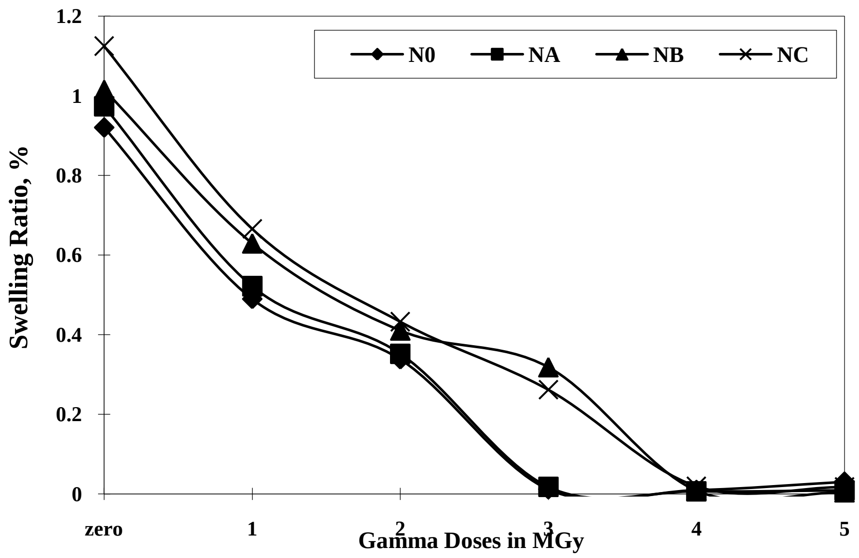


Fig. 4.1 Effect of Gamma Doses on Swelling Ratio of NBR samples with different Antioxidants

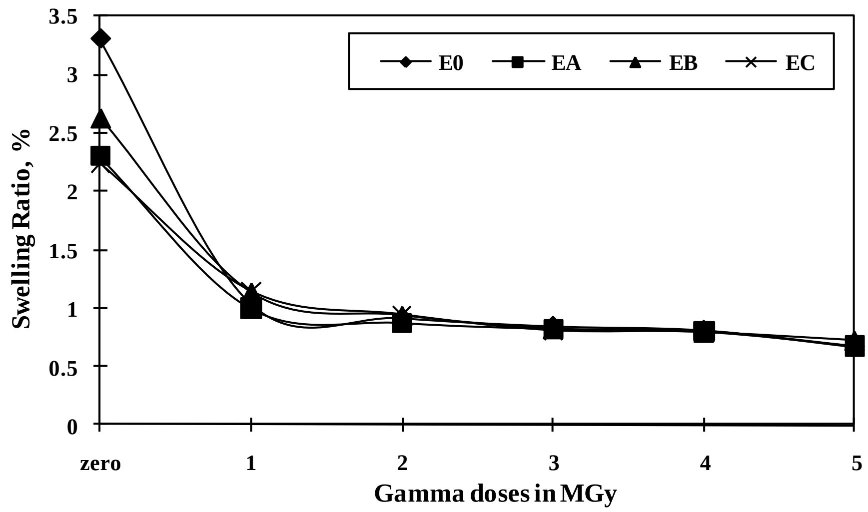


Fig. 4.2 Effect of Gamma doses on Swelling Ratio of EPDM samples with different antioxidants.

Fig. 4.4 shows a general trend in Crosslinking density and the molecular weight (Mw) are observed for EPDM rubber with different

PPDs antioxidants in comparing with EPDM rubber without any antioxidant. A sharp increase in crosslinking density is observed as the irradiation doses are increased from zero to 1MGy. Slight increase is observed with further increase in irradiation doses from 1 to 5 MGy. From this figure it is clear that there is a sharp decrease in the Mw of EPDM without antioxidants (EO) with increasing doses and for EPDM with different antioxidants the decrease is slightly.

4.2.2 Tensile Properties

Fig. 4.5 shows the effect of γ- irradiation dose on tensile strength at break (T_b) of different antioxidants PPDs in NBR samples. The tensile strength values of NBR without antioxidant (NO) are slightly increase with increasing the high doses till 1MGy, for further irradiation, it sharply decreases to the lowest value at 2MGy, then steeply increases again till reach the highest value at 5MGy. While T_b for NB has nearly the same value with increasing the dose up to 1MGy, then the T_b value tending to be brittle and the samples are deteriorated after 2MGy. For NBR with IPPD antioxidant (NA) and NBR with 6PPD antioxidant (NC) compound rubbers, T_b values decrease with increasing doses, NA samples deteriorate after 4MGy; while T_b value of NC increases after being exposed to 4MGy.

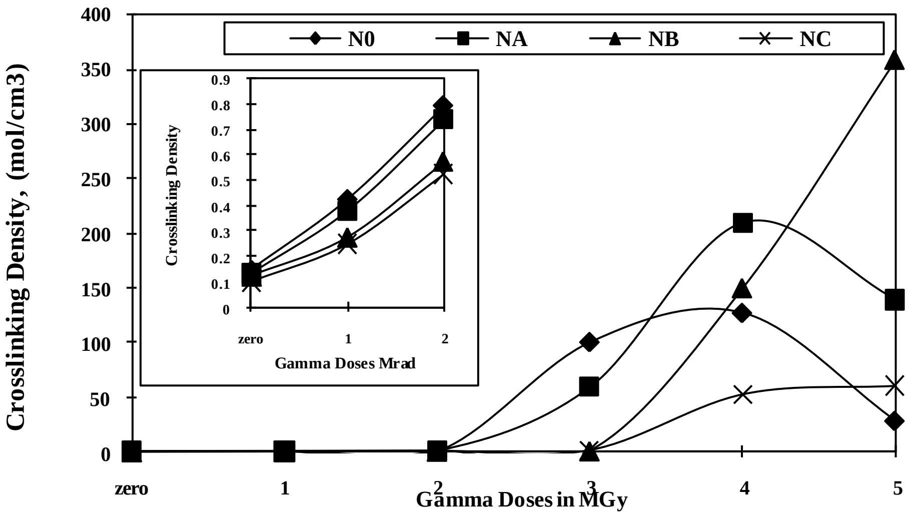


Fig. 4.3 Effect of Gamma Doses on Crosslinking Density of NBR samples with different Antioxidants.

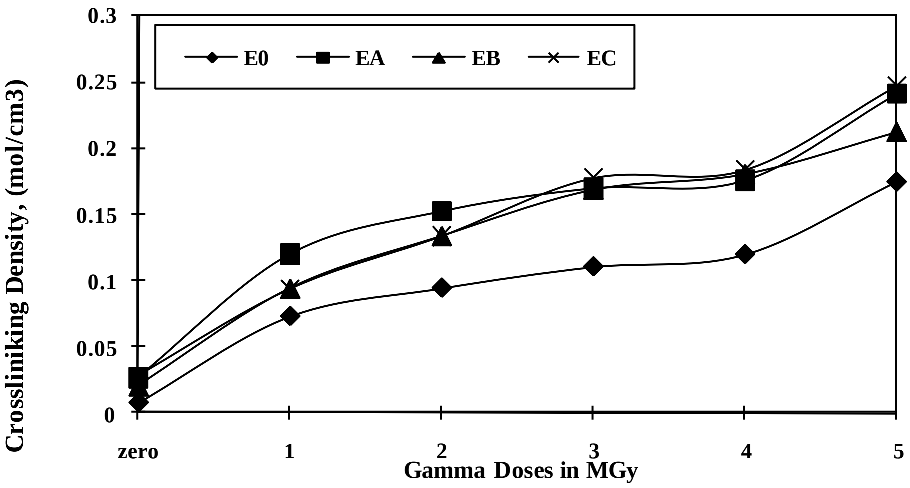


Fig. 4.4 Effect of Gamma Doses on Crosslinking Density of EPDM samples with different Antioxidants.

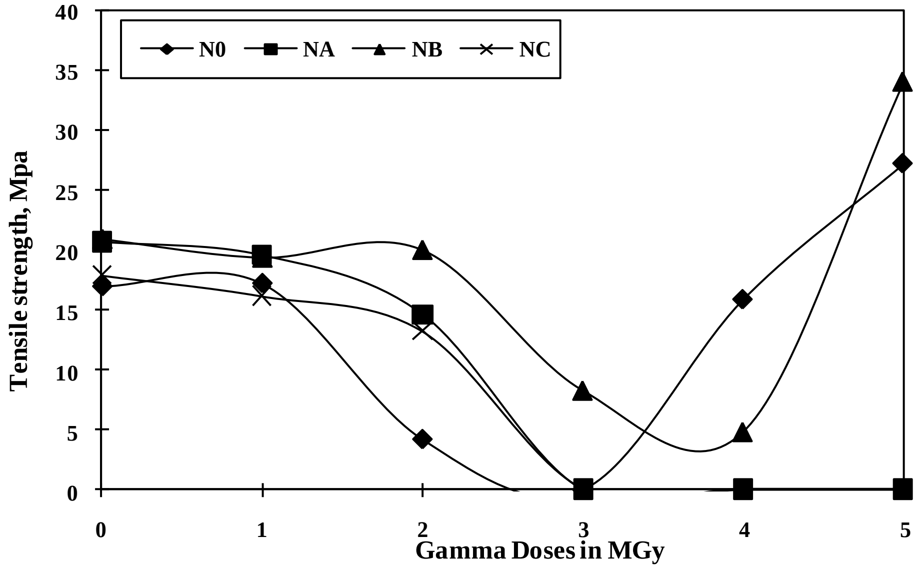
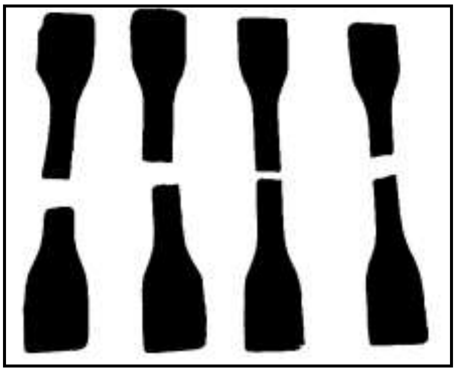
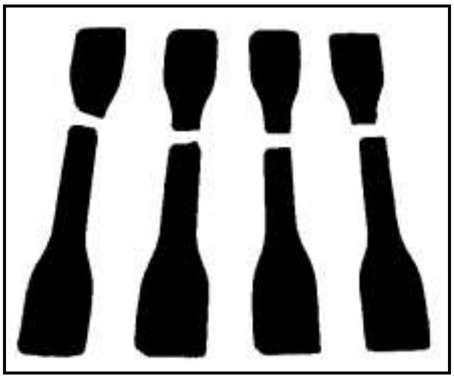


Fig. 4.5 Effect of Gamma Doses on Tensile Strength of NBR samples with different Antioxidants.



Unirradiated NBR samples after the tensile test (From the left to right: NO, NA, NB, and NC).



Irradiated NBR samples at 5 MGy after the tensile test (From the left to right: NO, NA, NB, and NC).

Fig. 4.6 shows the effect of γ-irradiation dose on tensile strength at break (T_b) of different antioxidants PPDs in EPDM rubbers. It can be observed that the tensile strength value of unirradiated EPDM without antioxidants (EO) has the lowest value, while unirradiated EPDM rubbers with PPDs antioxidants have relatively higher values than the EO rubber. The Tensile strength values steeply decreases when exposed to γ-doses up to 1MGy, this is observed for all EPDM rubbers, and then they slightly decrease with increasing the dose level from 1MGy till 5MGy value.

Fig. 4.7 shows the effect of γ-doses on the elongation at break (E_b) values for NBR rubber compounds with different PPDs antioxidants. The E_b values of unirradiated NBR rubber show that the NBR without antioxidant (NO) has the minimum value while the NBR with 6PPD antioxidant (NC) has the maximum value. E_b values for all NBR rubber compounds sharply decrease with increase of the γ-doses until 1MGy then all rubber compounds undergo deterioration.

Fig. 4.8 shows the effect of γ-doses on the elongation at break (E_b) on EPDM rubber compounds with different antioxidants PPDs. The E_b values of unirradiated EPDM compounds show that the EPDM with IPPD antioxidant (EA) has the minimum value. Also the figure shows there is enhancement in the (E_b) values for EPDM rubber with PBN (EB) and EPDM rubber with 6PPD (EC) up to 1MGy.

Fig. 4.9 shows the effect of γ-doses on Young's modulus (E). It is shown that the (E) values of all the NBR rubber compounds with PPDs

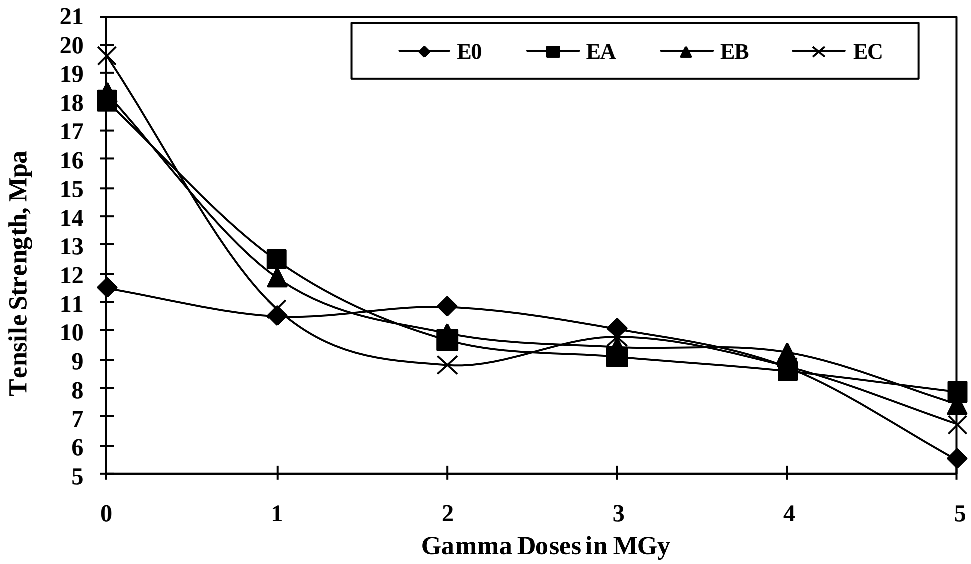
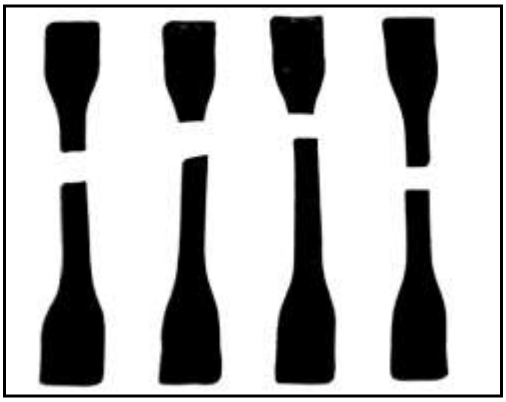
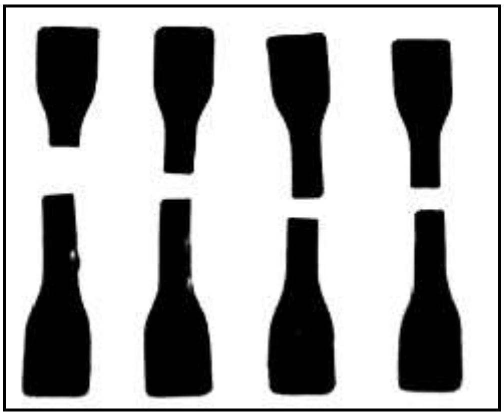


Fig. 4.6 Effect of Gamma Doses on Tensile Strength of EPDM samples with different Antioxidants.



Unirradiated EPDM samples after the tensile test (From the left to right: EO, EA, EB, and EC).



Irradiated EPDM samples at 5 MGy after the tensile test (From the left to right: EO, EA, EB, and EC).

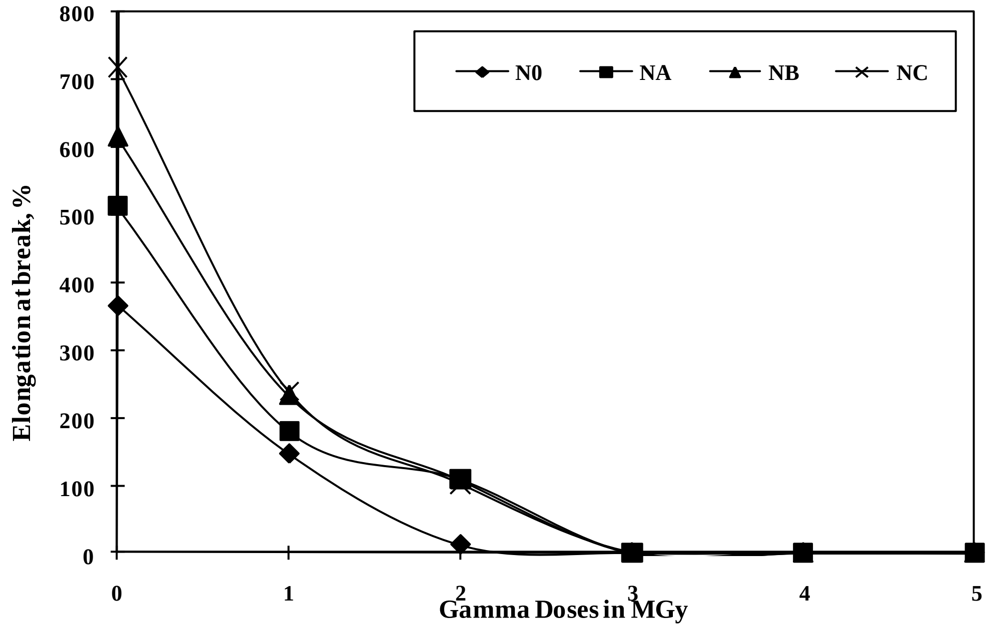


Fig. 4.7 Effect of Gamma Doses on Elongation at Break (%) of NBR samples with different Antioxidants.

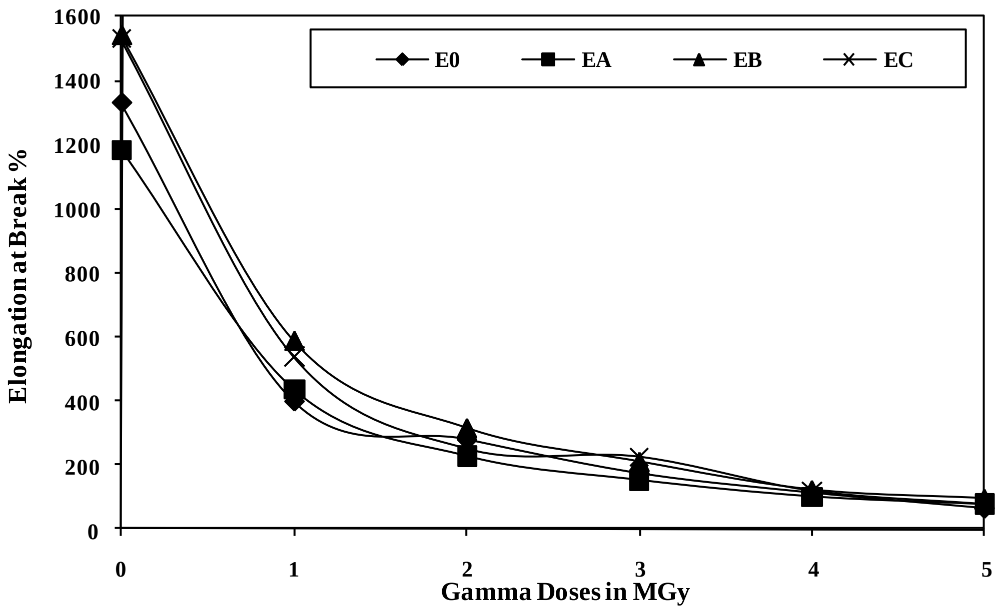


Fig. 4.8 Effect of Gamma Doses on Elongation at Break (%) of EPDM samples with different Antioxidants.

antioxidants have almost constant values up to 2MGy, while the (E) value for NBR rubber without antioxidants (NO) increases sharply.

Fig. 4.10 shows the effect of γ-doses on Young's modulus (E) on EPDM rubber with different PPD antioxidants s. It is shown that the values of (E) increase with increasing in γ-doses up to 5MGy for all of the EPDM compounds.

4.2.3 Hardness Measurements

Fig. 4.11 shows the effect of γ-doses on the Shore hardness for NBR rubber with different PPDs antioxidants. The figure shows that the unirradiated NBR with PBN antioxidant has the lowest value comparing with the others unirradiated NBR compounds. It is clear that the shore A hardness is used up to 2 MGy. For higher than 2 MGy the NBR compounds become so hard and brittle so that the Shore D hardness is used.

Fig. 4.12 shows the effect of γ-doses on the Shore hardness for EPDM rubber with different PPDs antioxidants. For all samples Shore A is used and the values of hardness steeply increase with increasing in γ-doses. It can be see from the figure there is enhancement in the hardness values for EPDM with PBN antioxidant (EB) and EPDM with 6PPD antioxidant (EC) at 1MGy.

4.2.4 Abrasion Resistance

Fig. 4.13 shows the variation of the abrasion rate of NBR rubber with different PPDs antioxidants as a function of γ-doses. It shows that for NBR without antioxidants (NO) the abrasion rate increases sharply with increasing γ-doses up to 3MGy. It can be seen that for NBR rubber

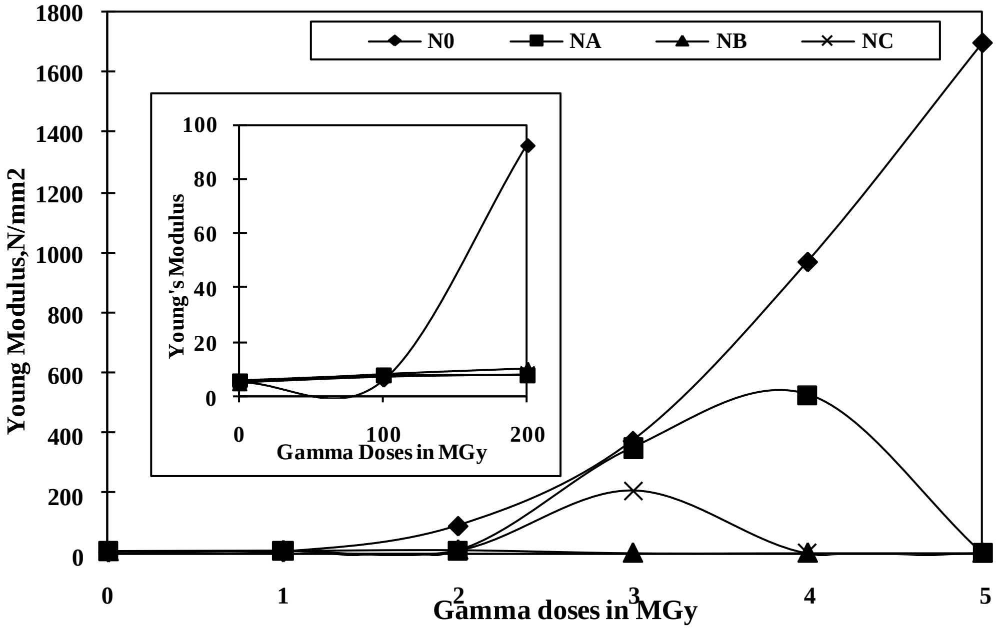


Fig. 4.9 Effect of Gamma Doses on Young modulus of NBR samples with different Antioxidants.

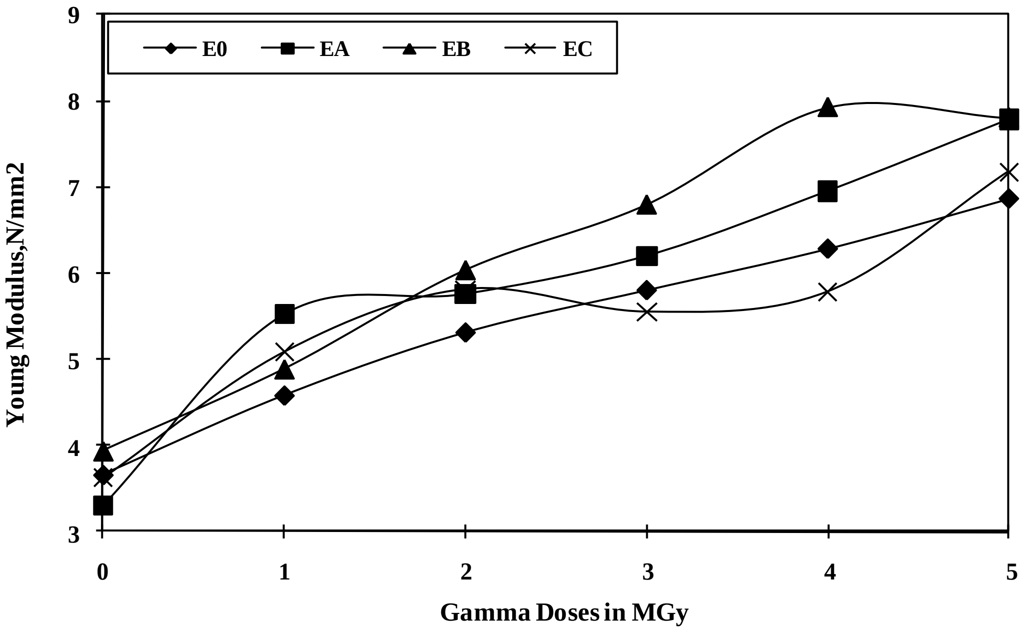


Fig. 4.10 Effect of Gamma Doses on Young Modulus of EPDM samples with different Antioxidants.

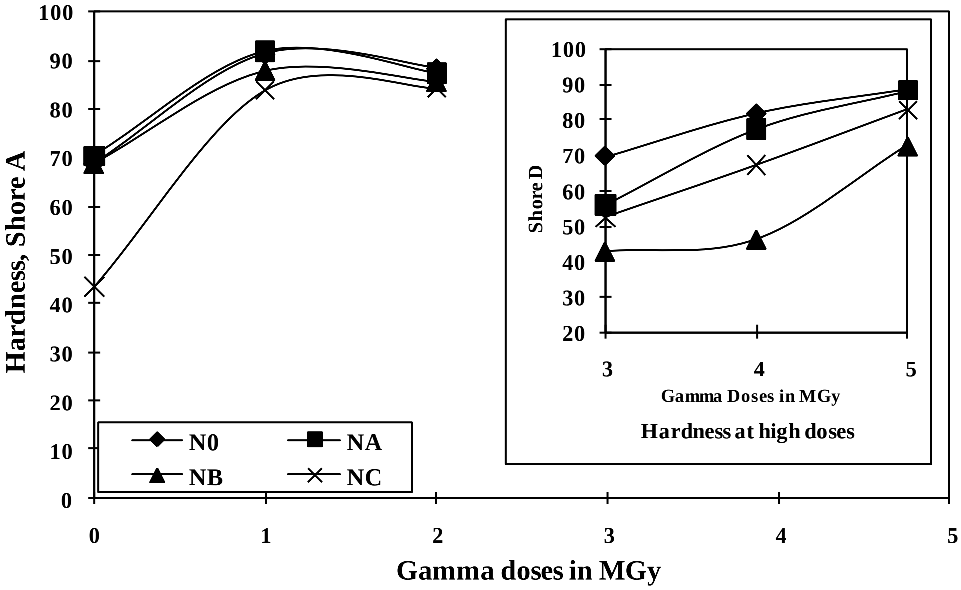


Fig. 4.11 Effect of Gamma Doses on the Hardness of NBR samples with different Antioxidants.

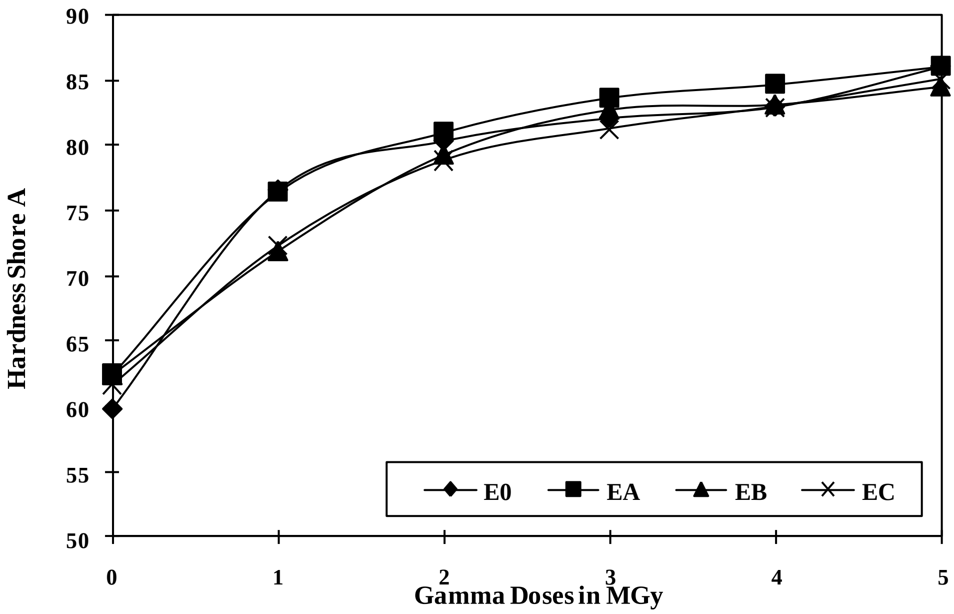


Fig. 4.12 Effect of Gamma Doses on the Hardness of EPDM samples with different Antioxidant.

with different antioxidants IPPD, PBN and 6PPD (NA, NB, and NC) respectively, the abrasion rate increases slightly up to 5 MGy.

Fig. 4.14 shows the effect of γ-doses on the Abrasion rate for EPDM rubber with PPDs different antioxidants. It shows that before exposure to γ-rays, EPDM without antioxidants (EO) has the high value of abrasion rate and the others EPDM compounds almost have the same value. At 1MGy there is a big drop of abrasion rate for EPDM without antioxidants (EO) which becomes almost the same with the others. After 1MGy the abrasion wears for all rubbers increase slightly with γ-doses increasing up to 5MGy.

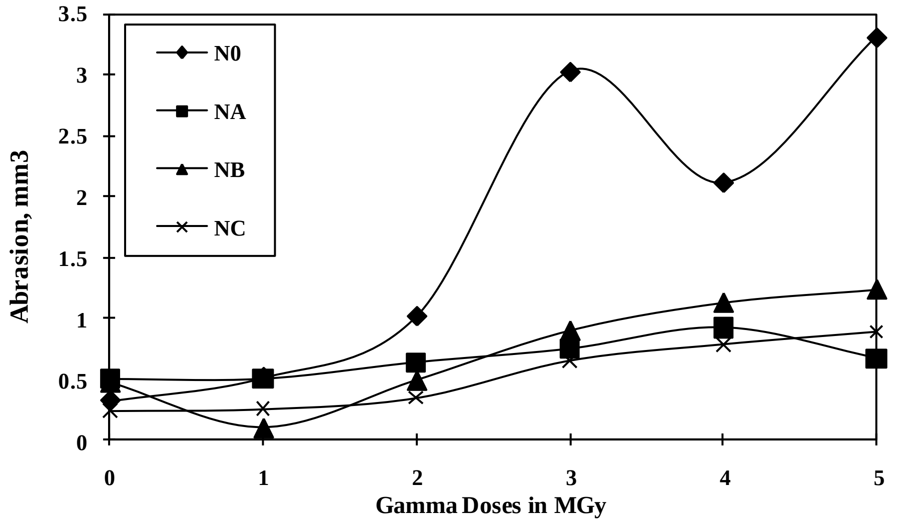


Fig. 4.13 Effect of Gamma Doses in Abrasion of NBR samples with different Antioxidants.

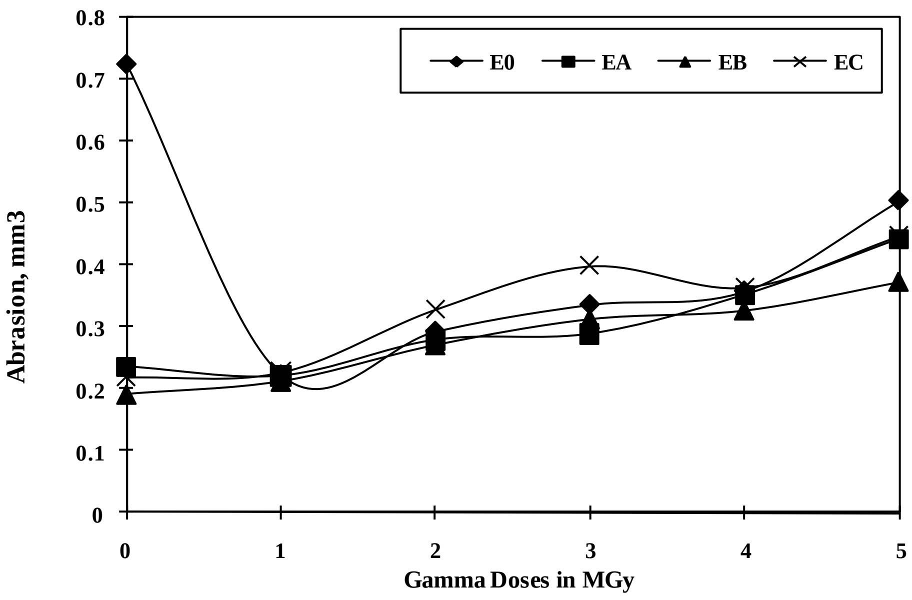


Fig. 4.14 Effect of Gamma Doses on Abrasion of EPDM samples with different Antioxidants.

4.3 Results of O-Ring Seals Measurements

4.3.1. Tensile Properties

Fig. 4.15 shows that the effect of high γ-doses on the tensile strength of NBR O-ring seals. It can be observed that generally the tensile strength decreases with increasing in the γ-doses. The two NBR O-ring seals with PBN antioxidant (NB) and NBR with 6PPD antioxidant (NC) have high values of tensile strength compared with the other two NBR O-ring seals without antioxidants (NO) and NBR with IPPD antioxidant (NA).

Fig. 4.16 shows that the effect of high gamma doses on the tensile strength of EPDM O-ring seals. It is observed that the tensile strength generally decreases with increasing in the γ-doses, for all the tested O-ring seals, for all tested EPDM O-ring seals. An EPDM O-ring seal without antioxidant (EO) has highest tensile strength value before and after exposing to gamma doses in compare to the studies EPDM O-ring seals with different antioxidants. EPDM O-ring seal with PBN antioxidant (EB) has the lowest value of tensile strength before and after exposure to gamma doses.

Figure 4.17 shows the changes in elongation at break for NBR O-ring seals exposed to the γ-doses. For all tested NBR O-ring seals exposed to gamma radiation, there is generally decreasing in ultimate elongation with increased of exposure doses.

The figure shows that the NBR O-ring seals with different antioxidants before the exposing to γ-doses have the highest value

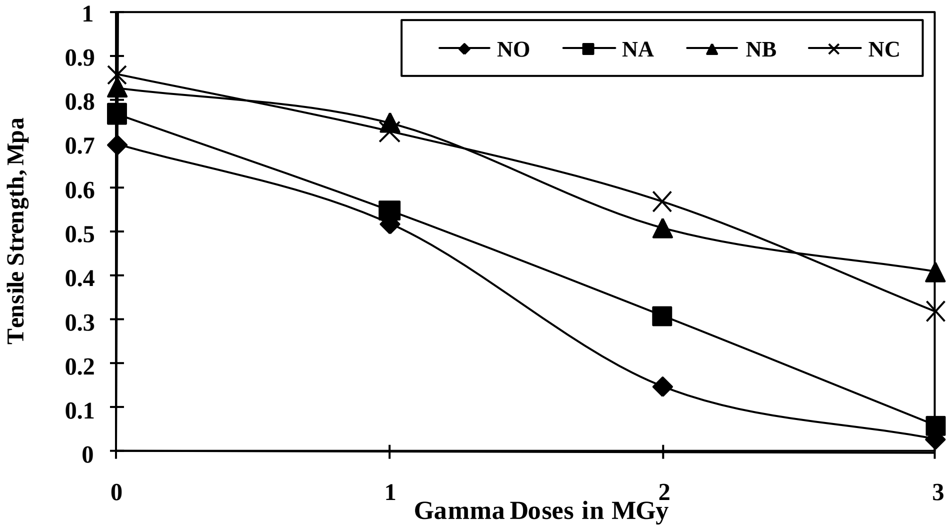


Fig. 4.15 Effect of Gamma Doses on Tensile Strength of NBR Seals with different Antioxidants

Unirradiated NBR o-ring seals after the tensile test (From the left to right: NO, NA, NB, and NC).

Irradiated NBR o-ring seals at 5 MGy after the tensile test (From the left to right: NO, NA, NB, and NC).

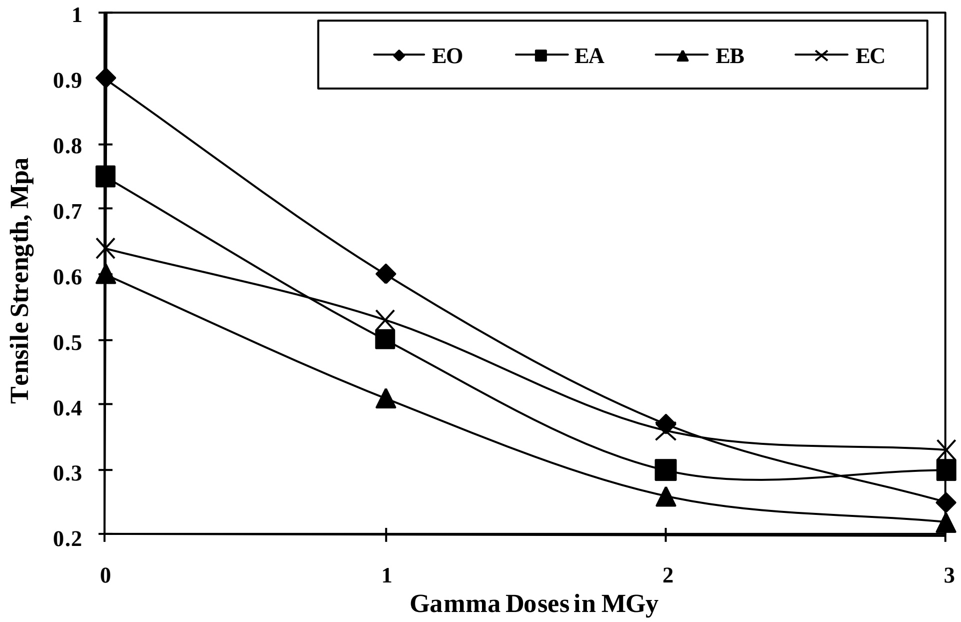
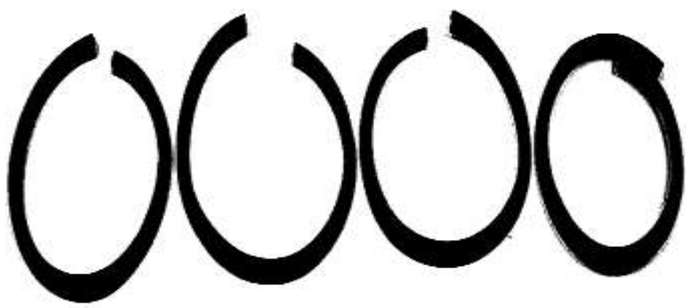
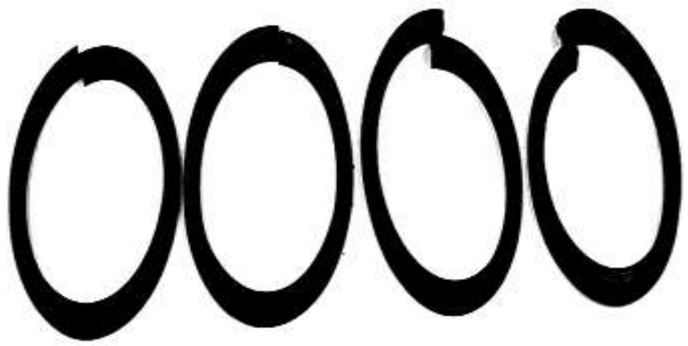


Fig. 4.16 Effect of Gamma Doses on the Tensile Strength of EPDM Seals with different Antioxidants

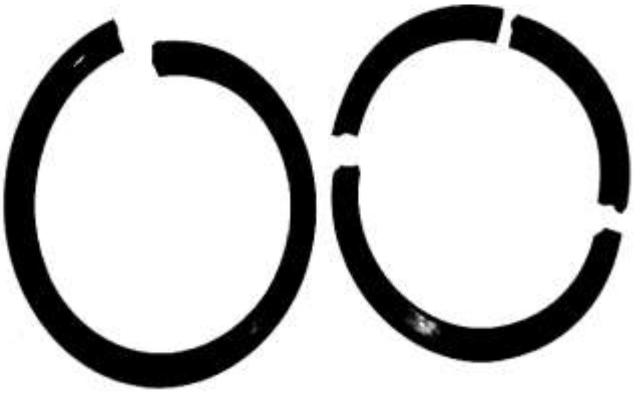


Unirradiated EPDM o-ring seals after the tensile test (From the left to right: EO, EA, EB, and EC).

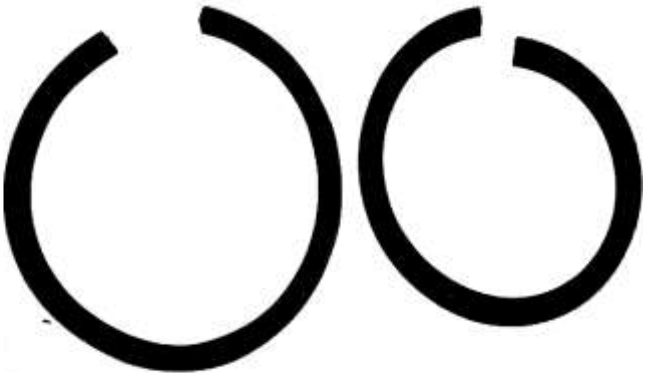


Irradiated EPDM o-ring seals at 5 MGy after the tensile test (From the left to right: EO, EA, EB, and EC).

Unirradiated EPDM O-ring seal (at the left) and EPDM O-ring seal at 3 MGy (at the right) after the tensile test.



Unirradiated NBR O-ring seal (at the left) and NBR O-ring seal at 3 MGy (at the right) after the tensile test.



Unirradiated EPDM O-ring seal (at the left) and the unirradiated NBR O-ring seal (at the right) after the tensile test.

comparing with NBR O-ring seal without antioxidant. NBR O-ring seal with PBN antioxidant (NB) and NBR O-ring seal with 6PPD antioxidant (NC) have highest elongation values after exposing gamma irradiation doses.

Figure 4.18 shows the changes in ultimate elongation for EPDM rubbers O-ring seals exposed to the three γ-doses. In general there was a decrease in ultimate elongation with increase γ-doses. EPDM O-ring seal with 6PPD antioxidant (EC) has the highest value before and after exposing doses up to 1 MGy in compare to the other studied EPDM O-ring seals. However, all studied O-ring seals after 1MGy showed significant reduction in elongation.

4.3.2 Hardness Measurements

Figs. 4.19 and 4.20 show the effect of γ-irradiation on the hardness of NBR and EPDM O-ring seals with different PPDs antioxidants respectively.

From figure 4.19 the value of hardness increases with increasing the γ-doses up to 1 MGy for all NBR seals, and then it decreases with increasing in γ-doses up to 2 MGy (i.e., becomes softer with increasing radiation dose).

Fig. 4.20 shows the effect of γ-irradiation on the hardness of EPDM O-ring seals with different PPDs antioxidants. The results show that the hardness value of EPDM O-ring seals increases with increasing

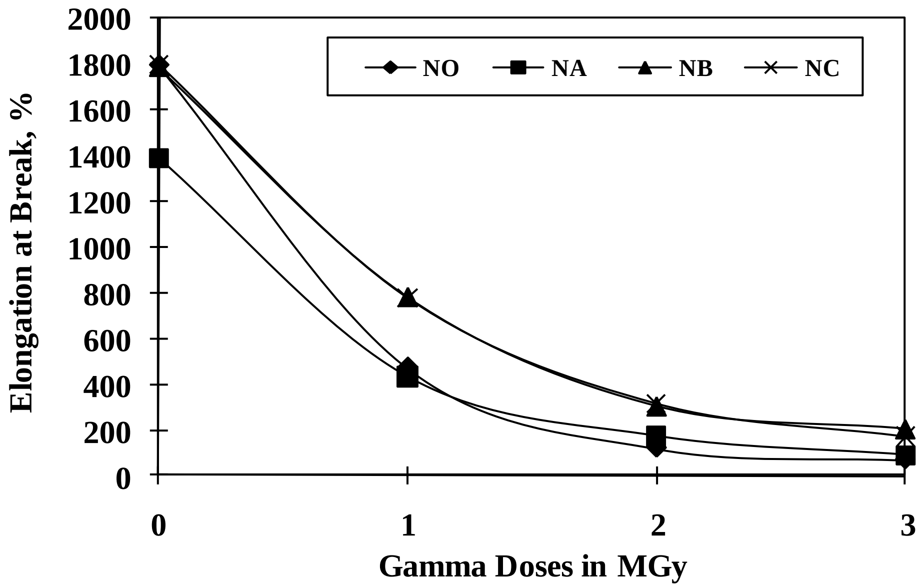


Fig. 4.17 Effect of Gamma Doses on the Elongation at Break of NBR Seals with different antioxidants

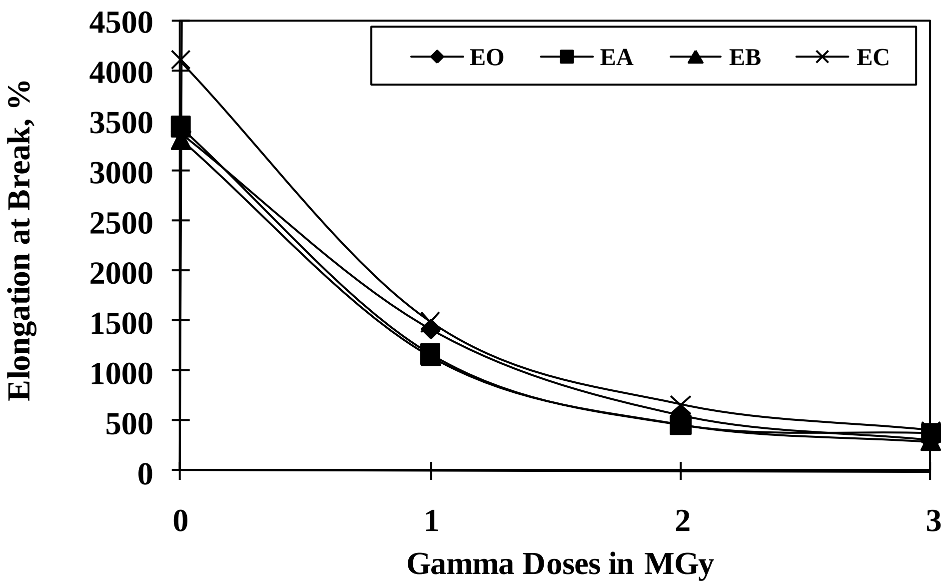


Fig. 4.18 Effect of Gamma Doses on the Elongation at Break of EPDM Seals with different Antioxidants

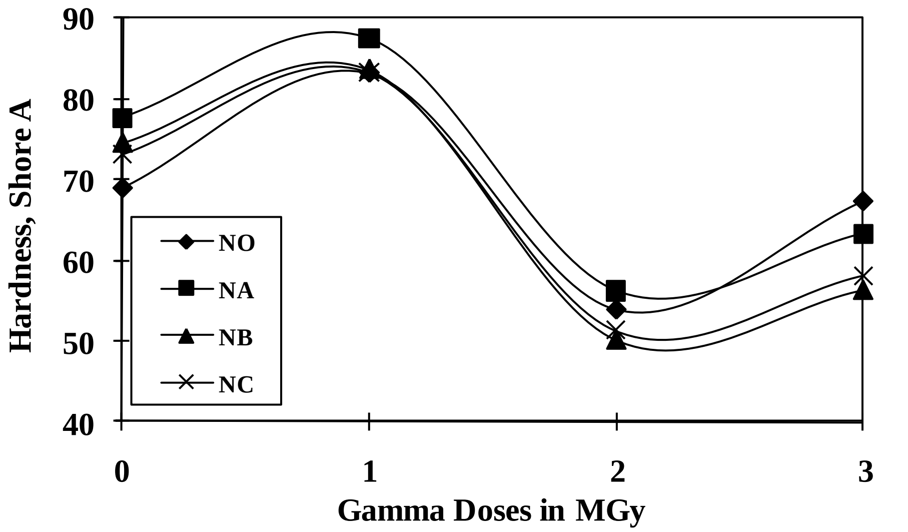


Fig. 4.19 Effect of Gamma Doses on the Hardness of NBR Seals with different Antioxidants

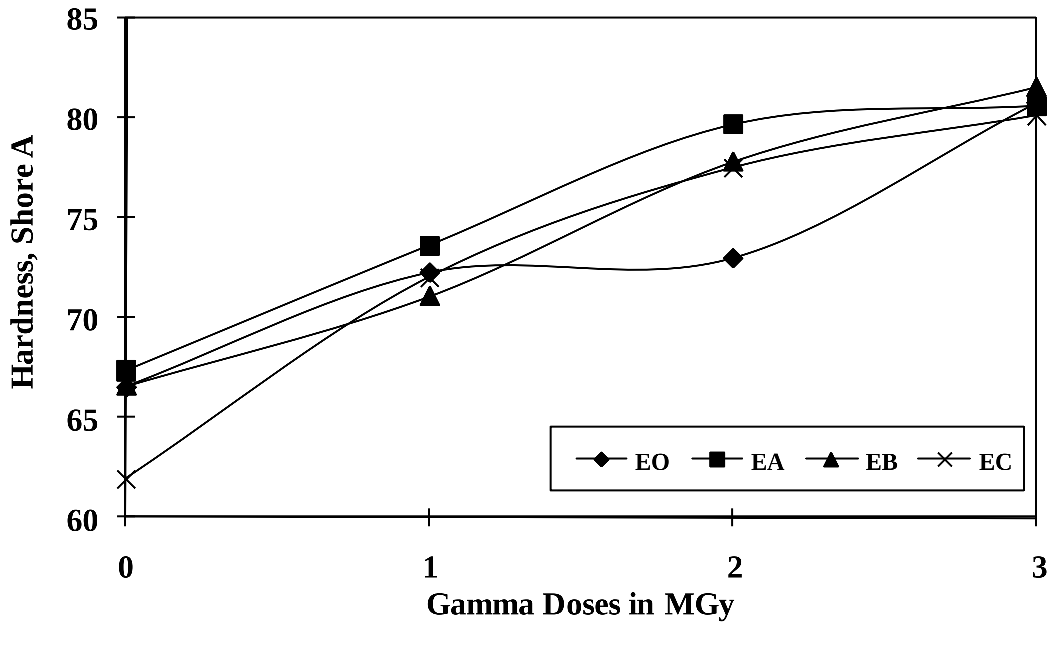


Fig. 4.20 Effect of Gamma Doses on the Hardness of EPDM Seals with different Antioxidants

the γ-doses up to 3 MGy. EPDM seals with 6PPD antioxidant (EC) have lower hardness value before gamma exposure in compare to other studied seals.

4.3.3 Compression Set (CS)

Figures 4.21 and 4.22 plot changes in compression set resistance versus radiation dose for NBR and EPDM rubbers O-ring seals respectively.

Fig. 4.21 shows that the Compression Set values for NBR O -ring seals before and after exposed to three γ-doses (1, 2, 3) MGy. From the figure the compression set values decreased sharply with increasing in the γ-doses up to 1 MGy.

Fig. 4.22 shows that the Compression Set values for EPDM O-ring seals before and after exposed to three γ- doses (1, 2, 3) MGy. The results show that the compression set generally decreased with γ- doses increasing. For unirradiated EPDM seals with IPPD antioxidant (EA) has the lower compression set compared with the others EPDM seals with antioxidants and at the high doses 3MGy EPDM seals without antioxidants (EO) has the highest compression set value.

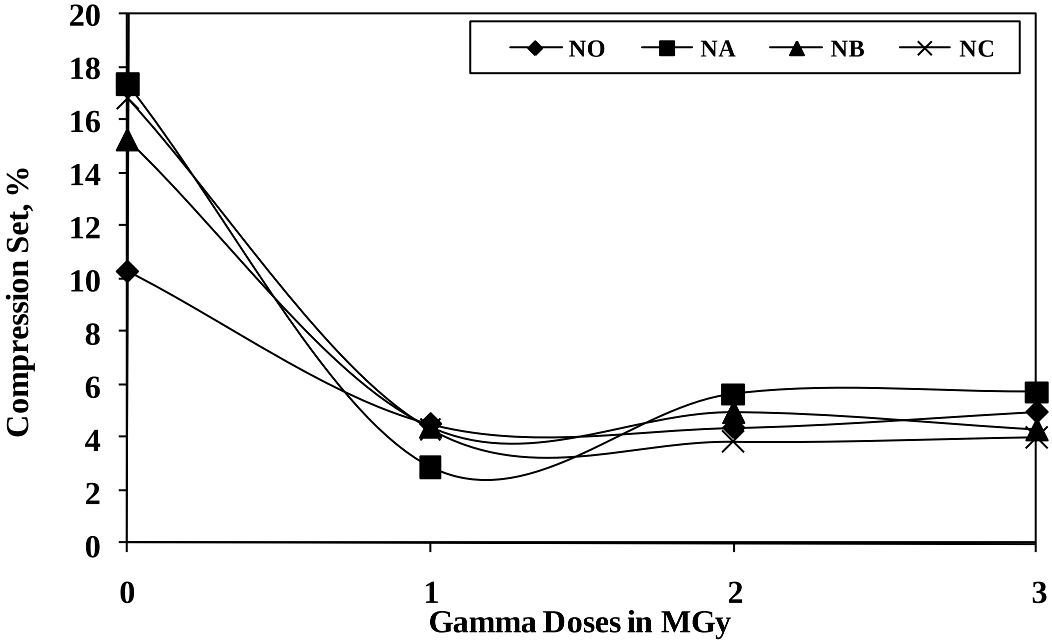


Fig. 4.21 Effect of Gamma Doses on Compression Set of NBR O-ring Seals with different Antioxidants

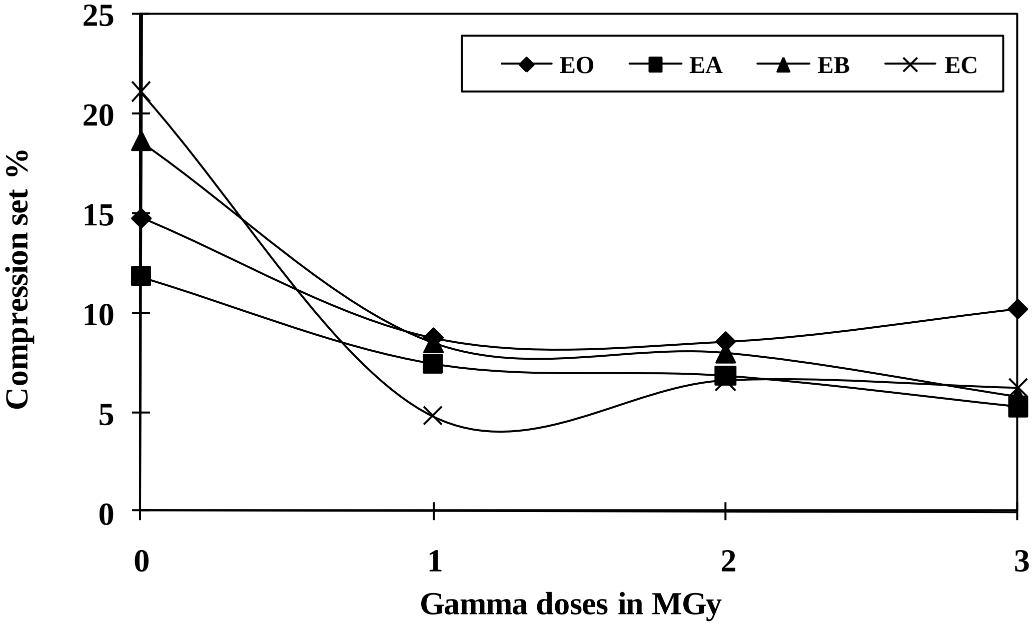


Fig. 4.22 Effect of Gamma Doses in Compression Set of EPDM O-ring seals with different Antioxidants