

Radiation Effects on the Thermal, Mechanical and Morphological Properties of High-Density Polyethylene/Ethylene–Propylene–Diene-Monomer Blend

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Abstract: Mixtures of high density polyethylene (HDPE) polymers with ethylene-propylene-diene terpolymer rubber (EPDM) were prepared in a Brabender Plasticorder PL2100 mixer at 180 ° C for a volume of about 200 cm³ and 10 minutes at 60 rpm. The mixtures were ionized using radiation to obtain the desired properties which are suitable for certain applications; especially in immature products such as kitchen utensils, toys, furniture, roofs, electrical and electronic products. The tensile strength, elongation, hardness, swelling behavior, thermal stability and surface properties (SEM) of irradiated HDPE / EPDM samples were examined for their content and compared with unexposed samples. The results showed that the tensile strength and the swelling resistance of the irradiated samples increased with increasing HDPE content in HDPE / EPDM mixtures and fracture elongation showed an opposite tendency. As the EPDM content increased, the modulus of elasticity decreased.

Keywords: Polymer Blends, EPDM, HDPE, Property, Ionizing Radiation.

INTRODUCTION

Polymeric mixtures are physical mixtures of homopolymers or copolymers of different structure. Over the past 40 years, a research on polymer blends has increased considerably. This is remarkable because the mixture has many important economic advantages. Since most polymer mixtures are processed with standard processing equipment, they can produce and / or process a material with unique properties that can improve and change the performance of expensive materials and increase the capacity of the material factory. It is known that the properties of polymer mixtures depend largely on the morphological phase (Abu Zeid, Shaltout, Khalil and El Miligy, 2008, Machado and van Duin, 2005, Rothon, 1995).

Because of their relatively low cost and their versatile properties, polyolefins are considered one of the main products of thermoplastic materials. As a result, mixtures have attracted a lot of attention (Zeid, 2007).

The market for ethylene-propylene-diene elastomers (EPDM) is growing rapidly. EPDM is obtained by polymerization with ethylene and propylene in the presence of a slightly unconjugated diene; this usually transmits many useful functions to EPDM. Some of these properties are good aging, good resistance to atmospheric agents and excellent resistance to ozone and oxidation without the use of anti-degrading elements. Other features including flexibility at low temperatures, color stability and ability to absorb large quantities of fillers, oils and chemicals.

In general, the external properties of rubbers with high diene content such as polybutadiene (BR), nitrile rubber (NBR), styrene-butadiene rubber (SBR) or natural rubber (NR) can be significantly improved by inclusion. low unsaturation tires such as ethylene propylene-diene monomer rubber (EPDM) (Corish, 1994, Mucha, 1976). EPDM elastomers are generally used for the production of joints, pipes (Rothon and Limited, 2003) and electrical insulators (Taherian, 2019). Since the EPDM is an important component of hydraulic-controlled machines and electric cables, the estimate of the duration in ionizing environments is of particular interest. Intact EPDM accelerates the degradation of polymeric

components. However, other results have shown that cross-linking reactions occur due to the sulfur atoms present in the vulcanized EPDM during the thermal hardening of EPDM.

Furthermore, the tensile strength and rigidity of EPDM increase at decomposition temperature (in the range of 100 to 180 ° C) (Gamlin et al., 2000). The spectroscopic study of thermal oxidation of EPDM showed that the glass transition of virgin EPDM was lower than the oxidized glass transition. This data indicates an increase in molecular weight during polymer degradation. It has been reported that thermal decomposition in air reduces the elongation at break of EPDM. Although thermally degraded and thermally degraded EPDM rubbers are subject to competition between fission and reactions.

Therefore, the effect of gamma irradiation on the mechanical properties of mixtures based on EPDM and EPDM based blends cannot be attributed to cleavage or cross-linking reactions. Non-linear effects were observed on some polymers (Ali, El-Nemr, Hamada and Abd-Elhady, 2017, Ali, El-Nemr, Hassan and Abd-Elhady, 2019). The interpretation of accelerated tests is therefore very complex and requires extensive research. Elongation at break is sensitive to irradiation by polymers and is therefore a valuable empirical criterion for estimating the durability of the polymer.

The mixture of hard thermoplastics, such as semi-crystalline HDPE with synthetic and completely amorphous soft rubbers like EPDM has been widely used in the production of polymers with various properties that can be used. mainly in the production of products without rice. Such a wide range can be extended by loading such mixtures of HDPE and EPDM with different compositions. These mixtures can be polymerized using chemical or radiation techniques. In this context, it is known that by cross-linking mixtures of polymers, materials that have better properties and greater stability can be produced after polymer exposure to aging, wear and aggressive media (Machado and Van Duin, 2005) HDPE and EPDM are both known to be exposed to cross-links when exposed to radiation due to their chemical structure (Wilski, 1987). This is due to the emergence of only 17% of the amorphous fraction in HDPE and to the limited amount of diene that provides some unsaturation in the EPDM (Mucha, 1976, Rothon, 1995). Therefore, it is possible to provide a limited amount of cross-linking if the HDPE / EPDM mixture is exposed to ionizing radiation.

The aim of this study is to study the effect of gamma radiation on the mechanical, thermal and physical properties of HDPE / EPDM rubber compounds. The physical and mechanical properties of HDPE / EPDM / MA blends are evaluated before and after exposure to gamma radiation. Furthermore, the morphological properties of the mixtures were examined by scanning electron microscopy (SEM).

EXPREMENTAL

Materials

The polymers used in the mixture were EPDM and HDPE. The EPDM rubber (Vistalone 5600) from Exxon Chemical in Belgium was obtained and its mixture content was kept constant at 50% (% by weight). HDPE was supplied by the Dow Chemical Company, in Spain. The density, melting temperature and crystallinity of the HDPE were 0.96, about 150 ° C and 94% respectively.

Blend Preparation

The preparation of HDPE / EPDM blends was carried out using a Brabender Plasticorder PL 2100 mixer with a working volume of 0.200 liters at 60 rpm. Various HDPE / EPDM compositions have been prepared. First, the HDPE was allowed to dissolve, then the EPDM was mixed in the device for about 10 minutes at a temperature in the range of 150 to 155 ° C to ensure a uniform distribution of the EPDM in the device. The hot mixture was then pressed at 10 MPa at 165 ° C for 5 minutes to obtain films of adequate size for analysis.

Gamma Irradiation

The mixtures were exposed to gamma radiation in environmental conditions. The total l doses administered were 0, 25, 50, 100, 150 and 200 kGy with a dose of 4 kGy / h.

Mechanical Tests

The tensile properties of the produced composites were determined using a Houns Fild computerized testing machine, England. To measure tensile strength, elongations in ISO 37-1977 (E) and ISO 34-1975 (E) were observed.

Thermal Analysis

The thermal behavior of all the synthesized mixtures was measured using a Shimadzu TGA-50 thermogravimetric analyzer (TGA) at a temperature between 20 and 600 °C at a speed of 20 °C / min.

Morphological Characterization

The ISM-5400 scanning electron microscope (JEOL, Tokyo, Japan) was used to examine morphological and gold fracture samples prior to the test.

Inflatable Tests

The swelling of the samples was measured using the following method. Three samples of approximately the same size and weight (~ 0.5 g) were accurately weighed (W) and immersed in 50 ml of solvent at room temperature for 24 hours. Each sample was then taken and placed between two pieces of filter paper. It was then placed between two 98.4 g glass plates for 5 seconds, then transferred to a bottle and weighed again (by weight). Swelling % ($Q\%$) was calculated using the following equation:

$$Q\% = \frac{W_t - W}{W} \times 100$$

In the above mentioned equation, W and W_t are the mass of the sample before and after the swelling respectively. The mass of the samples was measured with an electronic digital scale with an accuracy of 0.001 g.

RESULTS AND DISCUSSIONS

Mechanical Properties

Cleavage of weak macromolecular bonds is a common phenomenon in the treatment of radiation-induced polymers. The energy supplied by the radiation is absorbed by the exposed material that produces the stimulated macromolecules. These are fragmented and formed alkyl radicals. When the local oxygen concentration is sufficiently low, oxidative degradation progresses slowly. While it is known that the elastomers of ethylene and propylene belong to the class of cross linkable polymers, polyethylene is defined as air-soluble radiation at high doses.

Careful mixing of the polymeric components increases the risk of interaction between the macromolecules. In addition to recombination of free radicals, other reactions may occur during irradiation. Examples of these reactions are the disproportionate formation of double bonds and the extraction of hydrogen. Radiation increases the concentration of free radicals. In the case of EPDM / HDPE mixtures, it is very likely that the polyethylene degrades provides a higher alkyl content of elastomer (Machado and van Duin, 2005). Therefore, it can be understood that the polyethylene is "grafted" onto elastomer molecules.

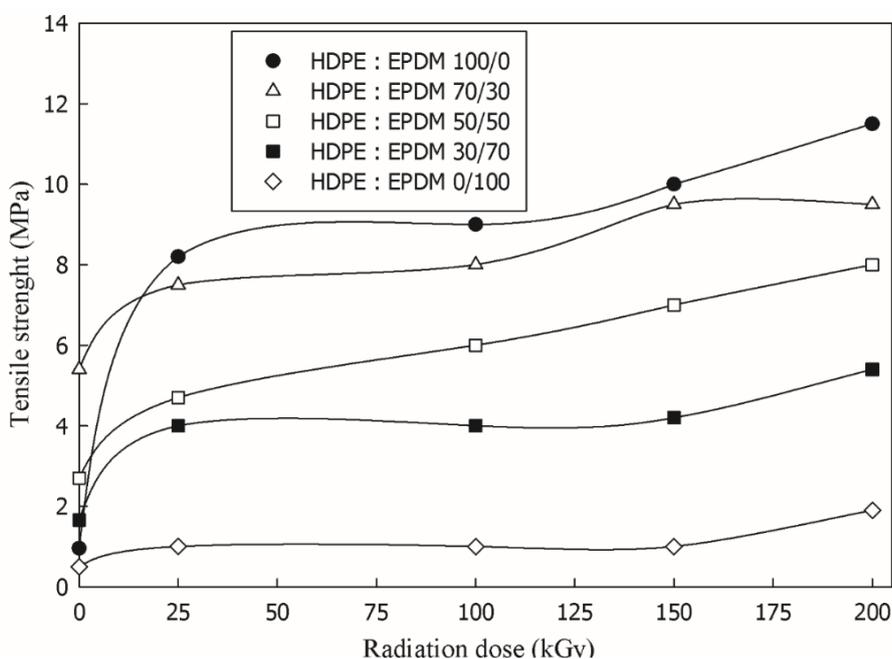


Figure 1: Variation of tensile at strength of HDPE blended with different composition of EPDM at various of gamma radiation doses

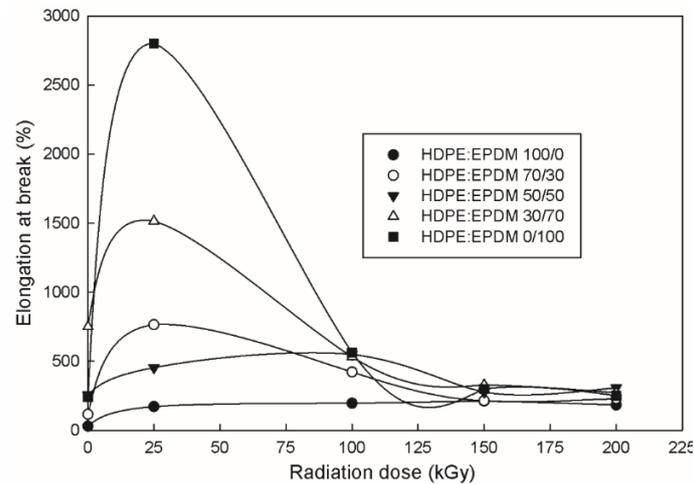


Figure 2: Variation of elongation at break of HDPE blended with different composition of EPDM at various of gamma radiation doses

Figures 1 and 2 show the results that obtained for the tensile strength and elongation at break of irradiated HDPE / EPDM mixture samples; having the following properties: 100/0, 70/30, 50/50, 30/70 and 0/100. The non irradiated results are also provided for comparison purposes. The presence of 30% (by weight) of EPDM in the mixture, causes an increase in shear strength and elongation compared to pure HDPE. This reduction is combined with the addition of 50% of EPDM. This behavior is expected because the tensile strength values of EPDM are lower than those of HDPE. However, a significant reduction in elongation at break of the mixture indicates that this system is incompatible.

The stress, which results as a function of the radiation dose of the mixtures, are also shown in Figs. 1 and 2. For all mixtures, the doses of 50 and 100 kGy have no significant effect on the mechanical properties EPDM is the most sensitive to radiation, as indicated by a reduction in elongation at break of over 40% to 40 kGy. In general, the data showed moderate to severe deterioration at 50 kGy. The reduction of the mechanical properties (observed at 30 and 50 kGy) can be attributed to the oxidative degradation of polymers in the presence of air produced by radiation (Song, Yoshino, Shibata, Nagatani and Ueda, 2009). However, antioxidants already present in polyolefins should reduce the oxidation rate. However, as irradiation progresses, antioxidants deteriorate due to partial radiolysis (Machado and van Duin, 2005). The degradation of antioxidants is influenced by various factors such as, the nature of the antioxidant and the polymer, the radiation dose and the dose ratio and the crystallinity of the polymer (Machado and van Duin, 2005, Wilski, 1987) it has been shown that the loss of crystallinity of the polymer derives from a greater oxidation potential due to the inability of oxidation to penetrate into the crystalline regions of the polymer (Song, et al., 2009). The breaking of polymer chains can reduce the resistance of polymers (Mucha, 1976). At 30 and 50 kGy, the mechanical property which was most affected by irradiation, was the elongation at break. This is consistent with Wilski's data (1987) according to which elongation at break is the most sensitive property to radiation. He also recommended using this parameter to assess the radiation stability of polymers.

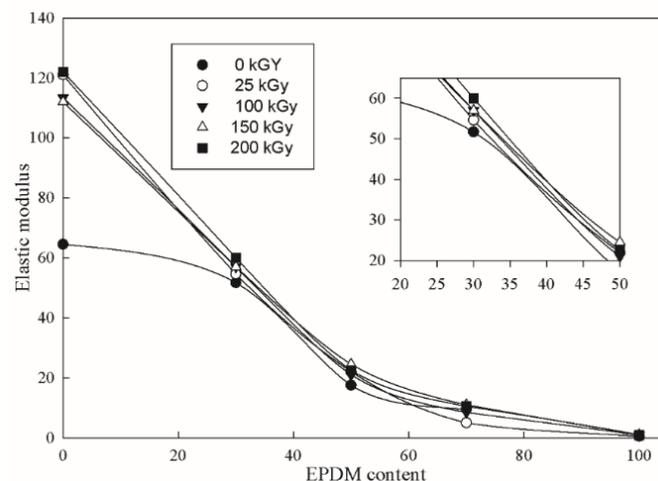


Figure 3: Variation of elastic modulus of HDPE blended with different composition of EPDM at various of gamma radiation doses

Figure 3 shows the flexibility module of HDPE / EPDM mixtures. It is clear that this module decreases as the EPDM content in the mixture increases. HDPE / EPDM blends with low EPDM content are characterized by the fact that the elastomeric phase remains in the form of dispersed particles. The smaller dimensions and the uniform distribution of the dispersed phase contribute to the higher flexibility module of the HDPE / EPDM mixtures. As the EPDM content increases, the agglomeration and therefore the particle-particle interaction of the EPDM explain the reduction of the modulus of elasticity of the HDPE / EPDM mixtures. This is a common observation because many researchers have reported similar results (Abu Zeid et al., 2008, Rothon, 1995). The presence of cross-linking HDPE and other hardening agents in the EPDM allowed the rubber particles to obtain greater stresses while imparting mechanical resistance to the particles (Mirzazadeh and Katbab, 2006).

Thermogravimetric Analysis (TGA)

The thermal degradation behavior of HDPE / EPDM mixtures has been studied by thermogravimetric analysis. TGA is one of the most used techniques to demonstrate the thermal stability of polymers in a given temperature range. The TGA thermogram for non-irradiated and irradiated mixtures with HDPE and EPDM is shown in Figures 4 and 5. Compatibility and polymeric / polymeric structure can influence the decomposition process. In general, thermal decomposition results from the combination of the effects of heat and oxygen. The decomposition temperature strongly depends on the weakest bonds and is produced by the loss of low molecular weight units (Feng, Hu, Yuan, Zhou and Zhou, 2002).

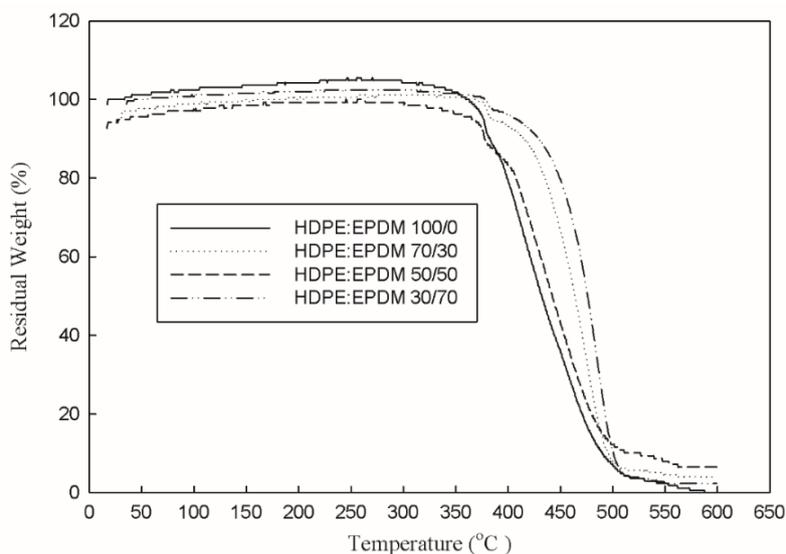


Figure 4: TGA thermograms of unirradiated HDPE blended with different concentration of EPDM

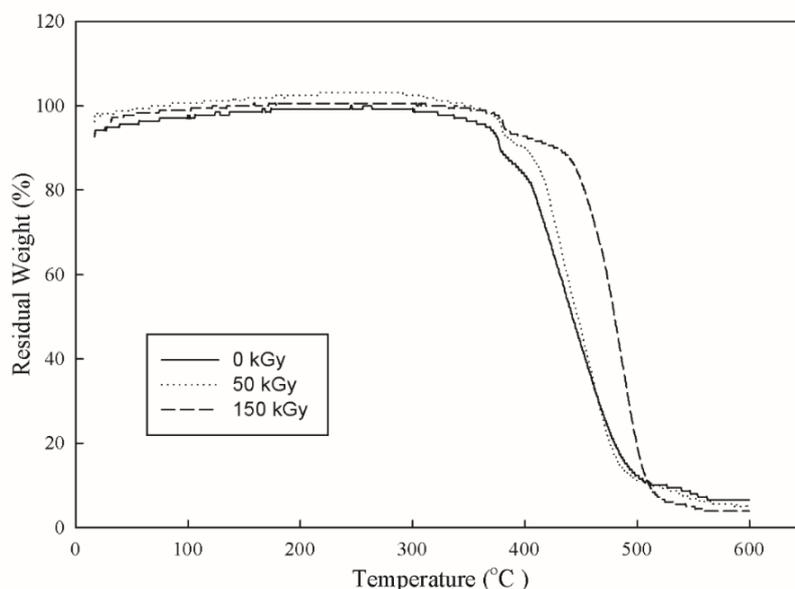


Figure 5: TGA thermograms of HDPE/EPDM, 50/50 wt% at various radiation doses

At thermograms, it should be noted that the final decomposition temperatures of the T (25) and T (75) mixtures increase with increasing EPDM content. The discovery of the contribution of EPDM to the improvement of the thermal stability of the mixtures has a higher thermal and thermal stability than HDPE. This result is due to the role of EPDM in the deactivation of HDPE macroradicals by intermolecular reactions (Pospisil, Horák, Kruliš, Nešpůrek and Kuroda, 1999).

Figure 5 shows the TGA curves of HDPE and mixtures exposed to 50 and 150 kGy. The figure also shows the effect of γ irradiation on the thermal behavior of the mixtures. The curves show that thermal stability increases with γ radiation. The positive effect of the β irradiation on the thermal stability of the mixtures can be explained by the increase in the compatibility and homogeneity of the polymer phases in the two mixture compared to the irradiation.

Kinetics of Thermal Decomposition

Activation energy For the thermal degradation of PE / EPDM mixtures, it was determined using only a heating rate and a mathematical equation. The results are shown in Table (1). The EPDM is likely to be two volatile products and a random chain failure during degradation. The values of the activation energy increase with the particle size, probably due to the diffusion mechanism of the degradation products, depending on the particle size (Paik & Kar, 2008). Calculated E_a values (Activation energy), It showed an unsystematic behavior for irradiated and irradiated samples. This behavior confirmed that more reactions occurred in the separation process.

Table 1: Activation Energy values of unirradiated and irradiated blends of PE/EPDM at different composition exposed to different gamma irradiation dose

Sample Composition (PE/EPDM)	Dose (kGy)	Activation Energy E_a (kJ/mol)
100/0	0	28.8
70/30	0	69.52
50/50	0	26.74
	50	31.7
	100	18.43
30/70	0	55.81

Development of Microstructures of Binary Polymeric Mixtures

X-ray diffraction (XRD) models of non-irradiated HDPE and their mixtures with EPDM are shown in Figure (6). Characteristic peaks of the isothermal model of crystalline orthophobic crystalline diffraction for HDPE in 2 θ ; The angles 21.40 (110) and 23.65 (200) were observed. The X-ray diffraction patterns of HDPE / EPDM mixtures show typical peaks of crystallographic planes, the orthophobic form of polyethylene superimposed on an amorphous halo (110) and (200).

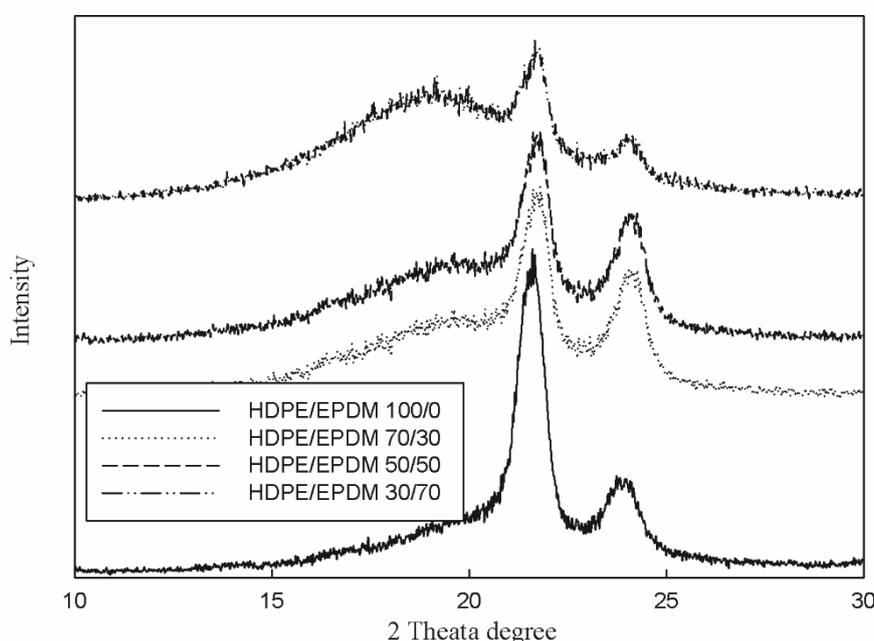


Figure 6: X-ray pattern of unirradiated HDPE blended with different concentration EPDM

The presence of these characteristic HDPE crystalline peaks in the mixtures clearly shows that the crystal structure of HDPE is intact during mixing, regardless of the amount of EPDM used. However, the peak density of crystalline HDPE in the mixtures decreases with increasing EPDM content. This variation in the height of the peak may be due to variations in the size or the average distribution of the spherulites, to the deformation of the boundaries of the spherulite or to the distant order induced by the dispersion of EPDM in the matrix of the HDPE structure. Here, elastomeric EPDMs can act as a nucleating agent for HDPE spherulites, influencing the crystal structure of HDPE (Moly, Radusch, Androsh, Bhagawan and Thomas, 2005).

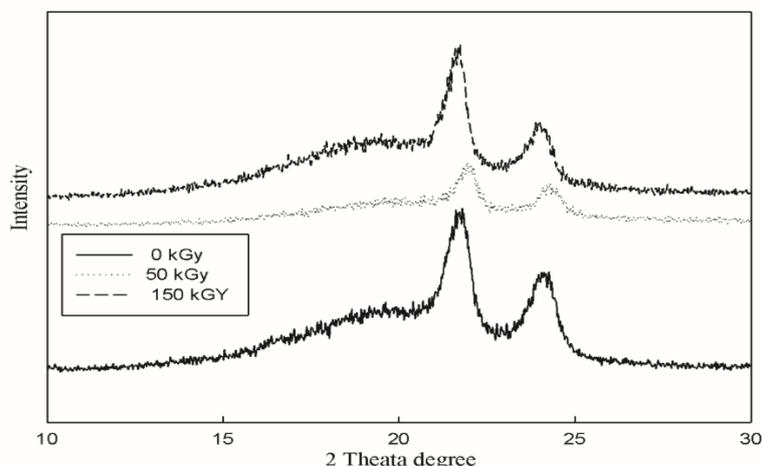


Figure 7: X-ray pattern of HDPE/EPDM,50/50 wt% blend with different gamma radiation dose

Figure 7 shows the X-ray diffraction pattern of the PE mixture before and after irradiation. The reflexes (110) and (200) of the orthophobic unit cells having a polyethylene structure were determined. There is no significant difference in the position of X-ray diffraction peaks of irradiated and irradiated mixtures. However, as the radiation dose increases, a general reduction of both reflectance intensities is observed. This shows the partial conversion of crystalline regions into unordered regions under the influence of gamma radiation (Miguez Suarez, Biasotto Mano and Abrahão Pereira, 2000).

Gel Fraction

The gel fraction (GF) is a useful technique to study the cross-linking or any type of cross-linking that can occur at the interface between the two phases of the polymer matrix. This technique provides a more complete picture of the mechanical properties, which implies the amount of crosslinking and degradation in mixtures that can occur under irradiation. The GF values of the HDPE / EPDM mixtures are shown in Figure (8) as a function of the radiation dose. These values increase with increasing irradiation dose due to cross-linking and due to irradiation. The observed increase in GF values. As the HDPE increases, this can be explained by the fact that the mixes are becoming more difficult with a low EPDM content. An alternative explanation is that in a high EPDM. This can cause a disparity, which in turn can lead to phase separation.

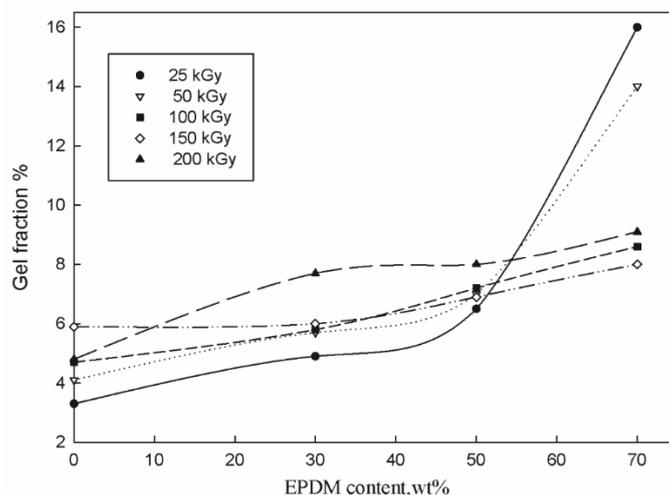


Figure 8: Variation of the gel fraction of the HDPE/EPDM blend with various irradiation dose

CONCLUSION

The present study describes the mechanical, thermal and morphological behavior of an immiscible mixture of HDPE and EPDM using the method of radiation crosslinking. In this mixture, the EPDM particles form the dispersed phase in the HDPE matrix. The presence of EPDM (30% by weight) in the mixture reduces tensile strength and elongation at break compared to pure EPDM. The most significant reduction in mechanical properties was observed at a radiation dose of 30 and 50 kGy. All radiated mixtures are thermally more stable than the corresponding one non-irradiated mixtures. The size of the main crystals of the mixtures increases with the dose of gamma radiation. By increasing the radiation dose, a cross-linked copolymer is obtained which minimizes the free space for swelling. SEM images support these results. At a relatively low radiation dose, no gelling was observed in the polymer mixture.

However, as the dose increases, the gel forms mainly in the HDPE matrix and residues can be seen in the hole and on the surface.

Gamma radiation destroys rubber because rubber is a type of polymer that can be easily crosslinked. Therefore, the cross-linking reaction must be carried out at a low dose. Cross-linking also reduces the number of double bonds and therefore the size of the rubber.

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