Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Online publication date: 11 December 2009

To cite this Article Shaltout, Nawal A.(2010) 'Effect of Electron Beam Irradiation and Ethylene Vinyl Acetate Copolymer on the Properties of NBR/HDPE Blends', Journal of Macromolecular Science, Part A, 47: 2, 160 — 165
To link to this Article: DOI: 10.1080/10601320903458671
URL: http://dx.doi.org/10.1080/10601320903458671

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2010) **47**, 160–165

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320903458671

Effect of Electron Beam Irradiation and Ethylene Vinyl Acetate Copolymer on the Properties of NBR/HDPE Blends

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Received May 2009, Accepted July 2009

The mechanical and physical properties of blends based essentially on nitrile butadiene rubber (NBR) and different ratios of high density polyethylene (HDPE) up to 25 parts per hundred part of rubber (phr) before and after electron beam irradiation were investigated. The values of tensile strength (TS), tensile modulus at 50% elongation (M_{50}), hardness and gel fraction % (GF%) of NBR/HDPE blends were increased with both irradiation dose and by increasing the content of HDPE in the blends. On the other hand, the values of elongation at break (E_b) were decreased with both irradiation dose and the content of HDPE in the blends. By loading NBR/HDPE (100/25) blend with ethylene vinyl acetate (EVA) copolymer the mechanical and physico-chemical properties were improved. Moreover, the degree of improvement is proportional to the loading content of EVA.

Keywords: NBR/HDPE blends, electron beam irradiation, ethylene vinyl acetate, mechanical properties, physico-chemical properties

1 Introduction

Blends based on thermoplastic and elastomeric materials would be expected to possess a wide range of properties depending not only on the properties of individual components but also on the additives, as well as the ratio of mixing. Such blends would have rubbery properties and at the same time they can be processed as a plastic material. Thus, substantial economic advantage is gained with respect to the fabrication of such elastomer/plastic blends into its end-use products (1).

NBR is an amorphous and polar synthetic rubber and does not undergo crystallization to any extent upon stretching. These properties, as well as acrylonitrile content, constitute the main parameters influencing the end properties of polymeric blend having NBR as a main component. Properties such as a faster cure rate, better heat resistance and resistance to permanent set would be expected to be imparted to such a blend. On the other hand, properties such as better resistance to chemicals and flammability, as well as higher impact strength and useful temperature range, are expected to be imparted to blends having HDPE as a main constituent. The end properties of prepared blends in the investigation depend not only on the properties and extent of either components, namely NBR and HDPE, but also to their susceptibility to undergo curing by electron beam irradiation. Crosslinking during radiation vulcanization of thermoplastic/elastomer blends may be considered essential for producing products with optimum properties (2).

The heat shrinkability of electron beam irradiated thermoplastic elastomeric films from blends of ethylene vinylacetate copolymer (EVA) and (LDPE) has been investigated (3)and radiation vulcanization of nitrile butadiene rubber/butadiene rubber blends was also studied (4). The results indicated that the addition of NBR has improved the properties of NBR/BR blends. Also, the NBR/BR blend is more thermally stable than BR alone.

The effect of different coagents on physico-mechanical properties of electron beam cured NBR/HDPE composites reinforced with high abrasion furnace (HAF carbon black) was carried out (5). Moreover, the effect of high energy electron beam irradiation on properties of nitrile butadiene/high density poly ethylene/carbon black composites was studied (6). The gel fraction of gamma irradiated LDPE/EVA blends, containing azodicarbonamide for the production of crosslinked foam was found to increase with increasing EVA content (7). Gamma irradiated, under argon, LDPE/EVA blends containing crosslinking agent, antioxidant, and flame retardant was studied, to improve their mechanical properties. The tensile strength and D hardness of the blends was found to increase with the irradiation dose (8).

A study dealing with the melt elasticity behavior and extrudate characteristics of LDPE/EVA blends was done

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(9). The results indicated that the melt elasticity of the blends increased with EVA concentration. These effects of high energy electron beam on LDPE materials containing EVA were followed (10). These results showed that EVA content of blends enhanced the sensitivity of the blends at lower radiation doses. The effects of the blend ratio, reactive compatibilization and dynamic vulcanization on the properties of HDPE/EVA blends have been analyzed (11). Moreover, the effect of electron beam irradiation on the properties of thermoplastic elastomer blends of epoxyed natural rubber/ethylene vinyl acetate was studied (12).

In the present work, NBR was blended with HDPE at different ratios up to 25 phr. A NBR/HDPE blend having 25 phr HDPE was blended with two different concentrations of EVA namely, 10 and 20 phr. The prepared blends were subjected to electron beam irradiation to doses up to 250 kGy. The mechanical and physical properties were studied as a function of irradiation dose, as well as the ratio of HDPE and EVA in the blends.

2 Experimental

2.1 Materials

High density polyethylene (HDPE) used throughout this work was supplied by Dow Company (Spain), had a density of 0.96 g/cm^3 and melt flow index of 2 g/10 min. Nitrile-butadiene rubber (NBR) was supplied by Bayer, Leverkusen, (Germany), commercial name (KRYNAC) 40–50, acrylonitrile content 40% by weight, density 0.98 (g/cm^3), mooney viscosity, ML 4 (100°C) 50 ± 5. Ethylene vinyl acetate (EVA) copolymer is a laboratory grade chemical, with 14% vinyl acetate content, melt index of 1.5 g/10 min. and it was provided by SNCI, France.

2.2 Preparation of NBR/HDPE Blends

The components NBR, HDPE and EVA at different ratios were mixed in a Plasticorder type 2100, made by Brabender Instruments, Germany, at 150°C at a mixing speed of 30 rpm for 10 min. After mixing, the blends were processed in two-roll mill (300 × 470 mm) with a gear ratio of 1.14:1 to obtain sheets of the blends. The blends were then compression molded into sheets of 1 mm thickness at 150°C under pressure of 15 MPa for 5 min.

2.3 Electron Beam Irradiation

Irradiation was carried out on the electron bean accelerator (1.5 MeV, 30 mA) facility installed at the National Center for Radiation Research and Technology, Cairo, Egypt. The required doses were obtained by adjusting the conveyer speed and current parameters to give a total dose of 10 kGy per each pass, in which the total irradiation doses of 50–250 kGy were obtained by multiple passes.

2.4 Determination of Gel Content

Samples of the prepared blends were accurately weighed (W_o) and then extracted with dimethylformamide (DMF) using the Soxhlet system for 24 h. After extraction, the samples were then removed and dried in a vacuum oven at 50°C to a constant weight (W_1). The gel fraction was calculated according to the following equation:

$$\text{Gel fraction } (\%) = (W_1/W_0) * 100$$

2.5 Mechanical Properties Measurements

Mechanical tests including tensile strength (TS), tensile modulus at 50% elongation (M_{50}) and elongation at break percent ($E_b^{\%}$) were performed at room temperature using an Instron Machine (model 1195, England) employing a crosshead speed of 50 mm/min. The recorded values for each mechanical parameter were the average of five measurements according to ASTM D-412-66T standards, in which the standard deviation was ±5%. The samples for tensile measurements were tested in dumbbell shape having a width of 4 mm and length of 50 mm.

2.6 Hardness Measurements

Samples of at least 1 mm thickness with flat surface were cut for a hardness test. The measurement was carried out according to ASTM D2240, 2000 using a durometer of model 306L type A Durometer from Pacific Transducer Co., Los Angeles, CA. The unit of hardness is expressed in (Shore A).

3 Results and Discussion

3.1 Mechanical Properties

Figure 1 shows the tensile strength (TS) vs. radiation dose for NBR and HDPE, as well as their blends at different compositions. It can be observed that the values of TS increase with increasing irradiation dose for all blend compositions to reach the maximum value at 150 kGy. At higher doses beyond 150 kGy, the values of TS started to slightly decrease with increasing irradiation dose. It can also be observed that two NBR have the lowest TS value and HDPE has the highest TS value, whereas the TS values of the blends displayed TS values between that of two components. The increase of TS due to electron beam irradiation indicated the occurrence of crosslinking, whereas the slight decrease beyond the dose 150 kGy indicated the occurrence of oxidative degradation. As already reported, HDPE is categorized as a crosslinking polymer. Moreover, it is already known that for semi-crystalline polymers such as PE, the crosslinking predominate at the interface between the amorphous and crystalline phases (13). After the crosslinking process, the density became high and the

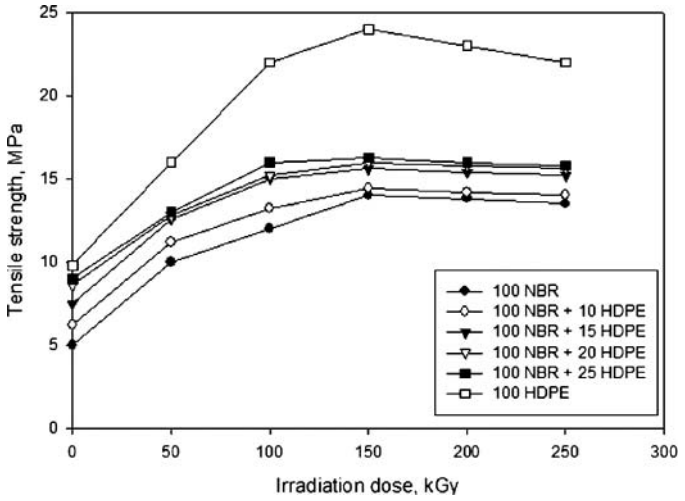

Fig. 1. Effect of irradiation dose on tensile strength of NBR, HDPE and their blends at different ratios.

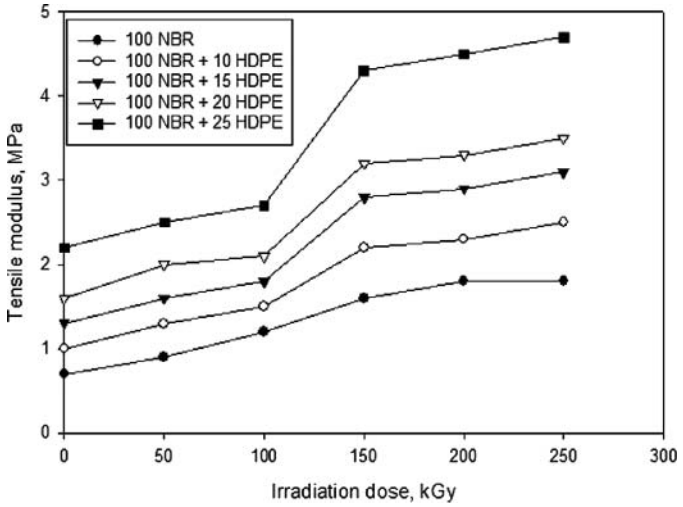

Fig. 3. Effect of irradiation dose on tensile modulus of NBR, HDPE and their blends at different ratios.

reorientation process was hindered and so the ability of micromolecules to crystallize or order was retarded. Under these conditions, the strength of the property was expected to decrease. Moreover, degradation of the constituents of the blend would be expected to predominate over crosslinking at such a high dose and would contribute to the decrease in TS values.

The effect of electron beam irradiation dose and EVA content on the tensile strength of NBR/HDPE (100/25) blend is given in Figure 2. It can be observed that the value of TS increased with increasing irradiation dose for all the blend compositions, reaching maximum values at 150 kGy and then decreased. The TS values of the blends also increased with increasing the content of EVA in the blends whether irradiated or unirradiated. An increase in the EVA content makes the blend more amorphous in nature, (14) which, in turn, increases its efficiency toward crosslinking at a particular radiation dose. It is known, EVA can easily form free radicals at lower radiation doses compared to PE (15). It can be observed that the TS value for NBR/HDPE (100/25) blend was 15 MPa, whereas the TS value for NBR/HDPE/EVA (100/25/20) is 30 MPa at 150 kGy.

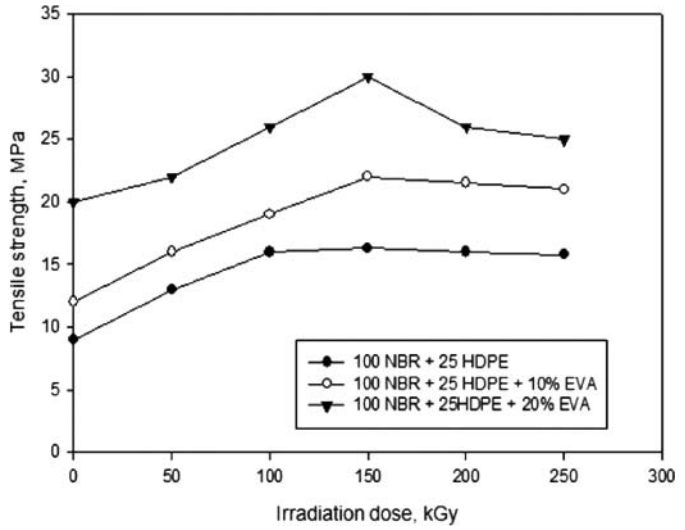

Fig. 2. Effect of irradiation dose on tensile strength of NBR/HDPE blends with different contents of EVA.

3.2 Tensile Modulus at 50% Elongation (M_{50})

The property that measures the resistance to limited strain deformation of polymeric materials under practical applications was the tensile modulus and it is known to be proportional to the stiffness. Figure 3 illustrates the effect of electron beam irradiation dose on the tensile modulus at 50% elongation (M_{50}) for NBR rubber and NBR/HDPE blends at different compositions.

It should be noted that the M_{50} values of the HDPE were not included as it ruptured before reaching 50% elongation as can be seen later in Figure 5. M_{50} values increased with increasing irradiation dose up to 250 kGy for all compositions. Moreover, the M_{50}values were found to increase with increasing the ratio of HDPE. The tensile modulus for systems of more than one component was known to be additive in nature, i.e., its value should be proportional to the sum of the modulus of each component multiplied by its weight or volume fraction (16). Radiation induced crosslinking and inter-phase linking would be expected to contribute to the M_{50} value, in which its magnitude increases with increasing irradiation dose.

The results showed that the modulus values increased with increasing irradiation dose, as well as EVA content in the blend; this behavior may be due to the increasing in crosslink density, and this can be seen in Figure 4. It can be noticed that the blend containing 20 phr EVA displays modulus strength values higher than that of the other two

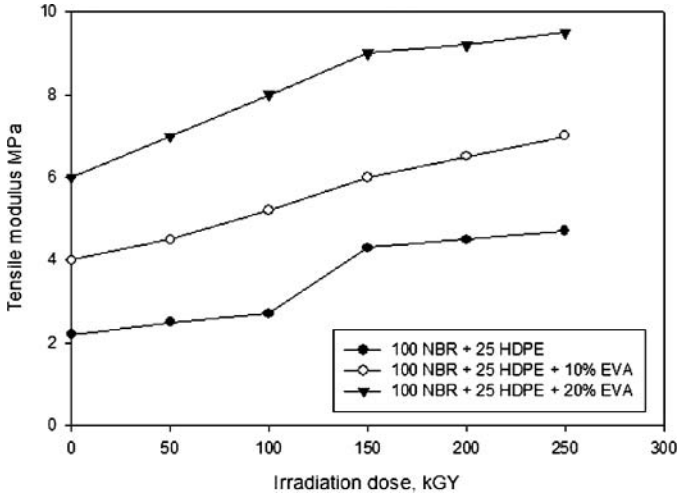

Fig. 4. Effect of irradiation dose on tensile modulus of NBR/HDPE blends with different contents of EVA.

compositions. Moreover, it was very important to notice that the presence of EVA had a great effect in improving mechanical properties of unirradiated blend, which in turn increase with increasing irradiation dose.

In Figure 5, the effect of electron beam irradiation dose on the elongation at break percent (E_b%) of NBR/HDPE blends at different compositions is given. It can be observed that increasing irradiation dose resulted in reduction in E_b for all compositions.

NBR is known to be a totally amorphous rubber having a bulky nitrile group and hence, its totally coiled-up structure with its considerably large physical entanglements would be expected to be effective in counteracting the effect of induced crosslinking and hence higher E_b values for NBR vulcanizates are expected.

HDPE has a high crystalline content of ~84% and a limited amorphous content. The induced crosslinking and the inter-phase induced chemical linking between the amorphous and crystalline regions took place. All these factors that accompany the effect of electron beam irradiation may contribute to the reduction of the values of E_b. While, E_b values of the blends showed E_b values between the lowest E_b values of HDPE and the highest values of NBR.

Figure 6 shows the effect of electron beam irradiation dose and EVA content on the elongation at break percent for NBR/HDPE (100/25) blend. It can be seen that increasing irradiation dose resulted in reduction in elongation at break of all the blend composition.

As the absorbed dose increased, the crosslinking density was increased leading to a reduction in the E_b. The E_b values of NBR/HDPE blends increased with increasing the contents of EVA in the blends, this increase in E_b values may be due to the high elasticity character of EVA. As the content of EVA increased the effective energy dissipation process became easier, which gave rise to an increase in the elongation at break.= (14).

3.3 Hardness Properties

The effect of electron beam irradiation dose on the hardness for NBR, HDPE and their blends at different compositions was studied and the results are given in Figure 7. With the exception of HDPE, the hardness values increased slightly with increasing the dose up to 250 kGy. The low hardness values attained of NBR were due to its structure. Crosslinking induced by radiation leads to an increase in the molecular weight of NBR and thus leads to a slight increase in harness. On the other hand, HDPE has a high degree of crystallinity and hardness is reported to be mainly

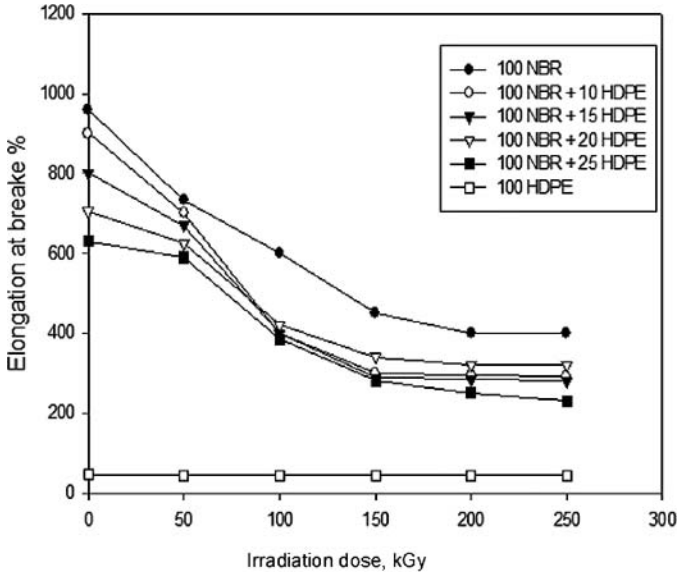

Fig. 5. Effect of irradiation dose on elongation at break of NBR, HDPE and their blends at different ratios.

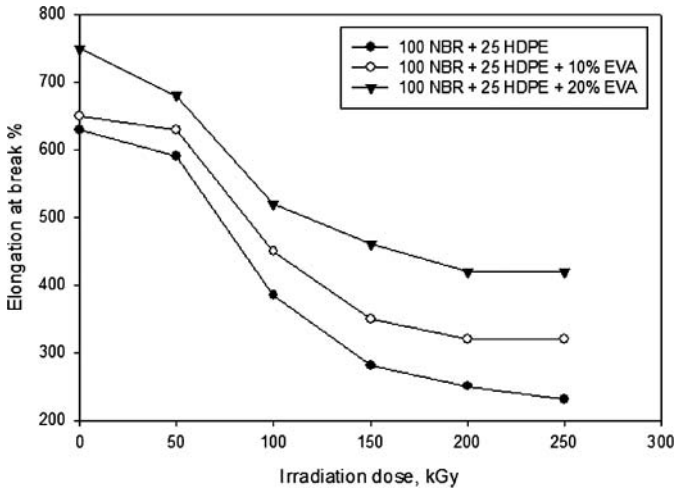

Fig. 6. Effect of irradiation dose on elongation at break % of NBR/HDPE blends with different contents of EVA.

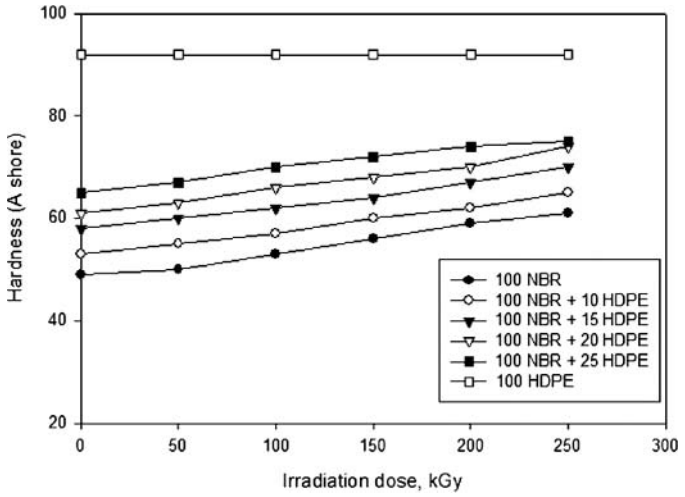

Fig. 7. Effect of irradiation dose on hardness of NBR, HDPE and their blends at different ratios.

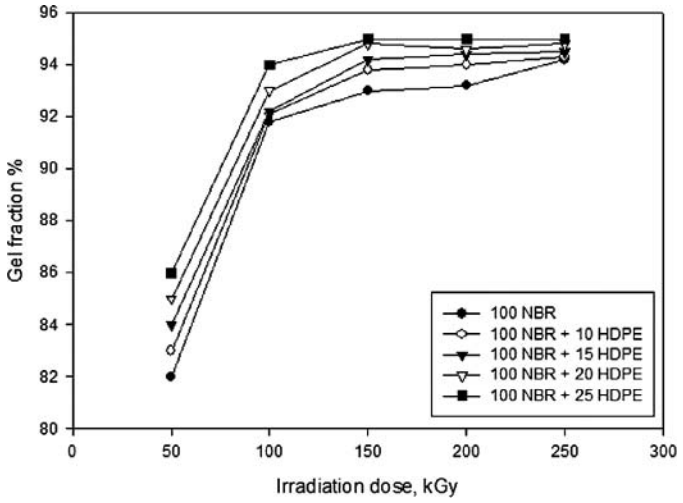

Fig. 9. Effect of irradiation dose on gel fraction of NBR, HDPE and their blends at different ratios.

a function of degree of crystallinity (17) and hence, relatively high values of hardness were obtained. Moreover, the increase in the content of HDPE in the blend would lead to an increase in its hardness, which is the case for the results obtained.

The effect of electron beam irradiation dose and EVA content on the hardness for NBR/HDPE (100/25) blend was studied. The hardness values increased again but slightly with increasing both irradiation dose and EVA content in the blend (Fig. 8). This behavior may be attributed to the increase in crosslinking density in the blend on loading with EVA.

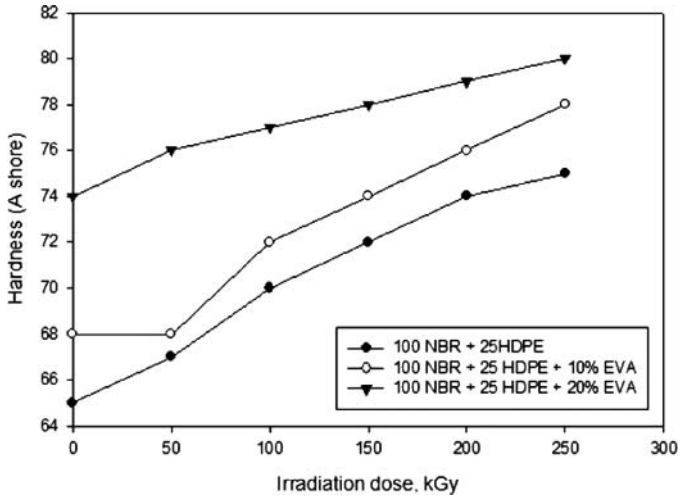

Fig. 8. Effect of irradiation dose on hardness of NBR/HDPE blends with different contents of EVA.

3.4 Physico-Chemical Properties

3.4.1. *Gel fraction*

The variation of gel fraction percentage GF% as a function of irradiation dose for the elastomer NBR alone, as well as its blends with the thermoplastic HDPE, is depicted in Figure 9. It may be observed that NBR has attained the lowest values of GF% over the whole irradiation range up to 250 kGy. Moreover, the GF% values for NBR, as well as its blends, have increased linearly and with a high rate on increasing the irradiation dose from 50 kGy to 100 kGy. A further increase of irradiation dose resulted in an additional increase in GF% values, but with a relatively slower rate. In addition, it may be seen that GF% values attained by the blends had increased systematically with increasing the content of HDPE in the blend when comparing these values at the same irradiation dose.

NBR is a totally amorphous and polar rubber and is categorized as a crosslinking type of polymer, though, on irradiation by accelerated electrons, some of its initial macromolecules are linked together by radiation-induced crosslinks thereby forming a three-dimensional network structure which may swell in DMF, but does not dissolve in it. The other part of NBR molecules that is not encountered in this process remains separated from the network structure, i.e., remained soluble and can be extracted from the bulk NBR by the proper solvent (18), namely DMF. Hence, the observed increase in GF% values of NBR with the increase of irradiation dose may be attributed to an increased rate of radiation-induced crosslinking leading to an insoluble network formation. Apparently, this process had taken place mainly in the lower irradiation range (from 50 kGy to 100 kGy).

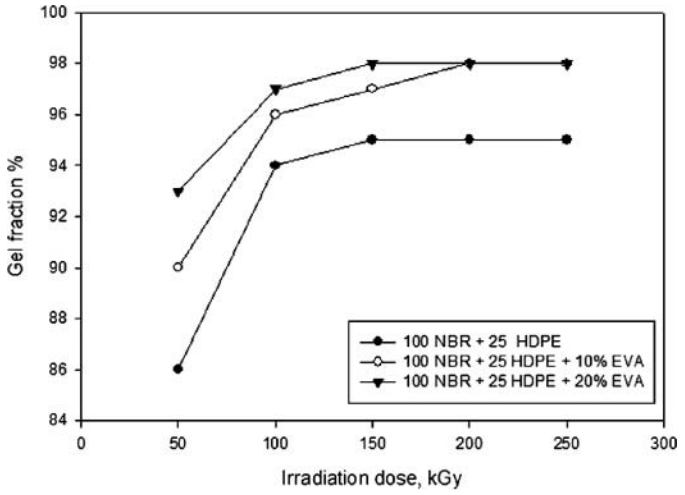

Fig. 10. Effect of irradiation dose on gel fraction of NBR/HDPE blends with different contents of EVA.

According to the above mentioned interpretation, it may be possible to assume that the magnitude of induced crosslinking has increased in blend compositions with respect to NBR rubber alone. Moreover, the extent of this increase is proportional to both the amount of HDPE in the blend and dose of irradiation. This assumption, however, has to be considered as in fact, the insoluble part, after extraction with DMF, is composed of not only the vulcanized part of NBR but also of HDPE. As a matter of fact, the higher the content of the latter, the lower the contribution from the former. One cannot however exclude the possibility of inter-phase induced crosslinking at the interface between the elastomer and the high crystalline part of HDPE as the free radicals formed at this interface is high.

From the above discussion, the GF% change with irradiation dose may be correlated mainly with extent of crosslinking in the case of the straight radiation vulcanization of NBR, whereas it may be correlated in the case of blends with induced crosslinking of NBR, effective types of chemical linking at the NBR/HDPE interface and nonsolubility of HDPE in DMF.

According to our observation, the gel fraction increases with increasing irradiation dose and the ratios of EVA. At the same irradiation dose, the gel content is found to increase with EVA ratios in the blends. As the irradiation dose increases, the probability of a generation of macro radicals increased, which in turn increases the gel content. EVA forms a large number of macro radicals under a similar dose because of elimination of the pendant acetate groups on irradiation. Hence, the content of EVA affects the gel content positively as shown in Figure 10. The increase of the gel content generally leads to the increase of elasticity of the polymer (19), which is in accordance with results of elongation at break, as shown previously.

4 Conclusions

This study has lead to the following conclusions:

- Radiation cured blends of NBR with limited amounts of HDPE has proper mechanical properties than NBR alone.
- Loading the blends with EVA improved the mechanical properties for the same irradiation doses.
- The gel fraction results showed that crosslinking is induced by electron beam irradiation in all samples.
- The gel fraction increased with increasing irradiation dose and EVA content of the blend.
- The thermoplastic/elastomer blend of NBR/HDPE (100/25) containing 20% EVA and cured with electron beam irradiation dose of 150 kGy exhibits good physicochemical and mechanical properties.
- This blend may be used in many industrial applications such as heat shrinkable material.

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