Effect of Electron Beam Irradiation on the Properties of High Styrene Rubber/Styrene Butadiene Rubber Blends

H. A. Youssef[a]

[a] Radiation Chemistry Department, National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt

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H. A. YOUSSEF*

National Center for Radiation Research and Technology, Radiation Chemistry Department, Nasr City, Cairo, Egypt

High styrene rubber (HSR)/styrene butadiene rubber (SBR) blends at different ratios were exposed to various doses of electron beam irradiation. The effect of irradiation dose and blend ratios on the mechanical properties and shape memory characteristics in terms of strain fixation) rate (R_f) and strain recovery rate (R_r) was investigated. The results revealed that rich styrene blends displayed higher tensile strength and hardness than low styrene content blends at all irradiation doses. However, elongation at break, and toughness were lower for rich styrene content. Also, it was observed that for most specimens, the tensile strength, elongation at break and hardness increases up to 100 kGy. Increasing irradiation doses resulted in slight deterioration in some mechanical properties only for low styrene content at 150 kGy. According to the normalized tensile stress at 25% elongation, it was found that the contribution of irradiation in enhancing the mechanical properties is higher for rich butadiene blends. On the other hand, it was observed that rich styrene content blends possess higher R_f and R_r at all the irradiation doses and stretching temperatures. However, the increase of irradiation dose decreases R_f values; the extent of this decrease depends on the blend ratios. Conversely, for all blends, R_r were increased by increasing irradiation dose and styrene content ratios.

Keywords: Electron beam irradiation, shape memory effect, mechanical properties, stretching temperatures

1 Introduction

Shape memory polymers are dual-shape materials. They have the capability of changing their shape upon external stimulus such as heat. First, the polymer conventionally processed to receive the permanent shape. Afterward, temporary shape can be obtained by heating up the polymer, deformation, and cooling the shape or drawing the sample at low temperature. Heating up the temporary shape above the transition temperature induces the shape memory effect. As a consequence, the recovery of the stored permanent shape can be observed. The netpoints determine the permanent shape of the polymer networks and can be chemical (covalent bond) or physical (intermolecular interaction) in nature. The physical crosslinking is obtained in a polymer whose morphology consists of at least two segregated domains as found in block copolymer. Shape memory effect is not an intrinsic property, i.e., not related to a specific property of a single polymer; it is rather a combination of polymer structure and polymer morphology together with the applied processing and programming technology (1). Shape memory effect can be observed for several polymers that may be different in their structure (2–7). Together with polynorbrene and polyethylene, styrene butadiene rubber was one of the first polymer reported to exhibit the shape memory effect (8). Styrene butadiene block copolymer made of high ratio 1,4- trans polybutadiene (34%) and polystyrene (66%) are found to be semicrystalline (9) The melting temperature of polybutadiene crystalline represents the switching temperature for a thermally shape memory where polystyrene supplies the hard segments determine blocks. The high glass transition of polystyrene blocks hinders polybutadiene chains from slipping off each other upon stretching. The elastic properties are not only responsible for elastic strains, but also for recovery attributed to the amorphous area of the polybutadiene phase. Shape memory polymers are a class of polymers with applications spanning various aspects of everyone's life. For example, such application can be found in smart fabrics (10,11), heat shrinkable tubes for electronics or films for packages (12), intelligent medical devices (13), or minimally invasive surgery (14,15). In this article, high styrene rubber (HSR) and its blends with SBR, (23% styrene) by different ratios, are exposed to different irradiation dose, consequently, chemical crosslinks are created between its chains. Therefore, a combination of physical netpoints and chemical crosslink in HSR is expected to improve the mechanical, as well as the shape

*Address correspondence to: H. A. Youssef, National Center for Radiation Research and Technology, Radiation Chemistry Department, Nasr City, Cairo, Egypt. E-mail: amer05ali@yahoo.com

memory characteristics of the specimens under investigation.

2 Experimental

2.1 Materials

All the materials used in this work are of commercial grade. High styrene rubbers (HSR), Nipol HS680 with 60% styrene content, 53 Mooney viscosity, 0.98 g/cm² density, and 70–90°C heat distortion temperature (HTD), styrene butadiene rubber (SBR) 1502 (23.5% styrene). The blends of HSR with 25, 100, 150, and 200 phr SBR correspond to 53, 48, 38 and 35 % styrene content, respectively.

2.2 Preparation of HSR/SBR Blends

HSR was passed, first compounded through a laboratory roll mill, several times at an opening about 0.2 mm. Three to four cuts were made every half minute from each side alternatively, and the roll temperature was maintained at about 60°C. SBR was then introduced and the average total time of mixing was 10 min. A sheet of 2 mm in thickness was obtained by an clean mold of an electric press. The molds were set to 160°C and held at this temperature for 5 min and a pressure of 6 MPa on the mold surfaces.

2.3 Electron Beam Irradiation

Irradiation of the samples was carried out an using electron beam accelerator ICT type supplied by High Voltage, USA, 1.5 Mev energy, 30 kw power, 25 mA beam current and scan width up to 90 cm. Irradiation was proceeded several times under atmospheric conditions at 5 mA beam current and every pass resulted in 25 kGy to avoid sample heating.

2.4 Mechanical Measurements

Specimens were cut in the form of five individual dumbbell-shapes using a steel die of a standard width 6.25 mm. The ultimate tensile strength, tensile modulus, elongation at break point were determined at a crosshead speed 50 mm/min on a rubber tensile testing machine H10 KS, Qmat 3.92 Hounsfield, Germany.

The tensile stress at a given elongation and the degree of crosslinking is expressed according to the following equation (16).

$$F/A_o = \rho RTMc^{-1}(\lambda - \lambda^{-2}) \qquad (1)$$

Where A_o is a cross-sectional area, F is the force required to produce an elongation λ, ρ is the density of the rubber, R is the gas constant, T is the absolute temperature, and Mc is the molecular weight between crosslinks. When ρ, T, and λ are kept constant, then F/A_o depends on Mc^{-1}, i.e., the stress at definite elongation is inversely proportional with Mc.

2.5 Shape Memory Measurements

2.5.1. *Strain fixation rate (R_f)*

Dumbbell shaped specimens (1.27 cm width) with 5 cm bench mark were heated at 60, 70, and 80°C using a heating gun, then stretched to 100% of bench mark using tensile machine type (Hung Ta Instrument Co., LTD, HT-9112 Taiwan) at a stretching rate of 50 mm/min. The samples were then cooled by water spray in stretched conditions, the stress is released and left for 24 h to allow for elastic rebound.

The strain fixation rate (R_f) describes how exactly the sample can be fixed in the stretched shape after a deformation. The resulting temporary shape always differs from the shape achieved by deformation. R_f is given by the ratio of sample strain after cooling and stress release (ε_u) to that strain under stress (ε_m) as follows:

$$R_f = (L_t - L_o)/(L_s - L_o) \times 100 = (\varepsilon_u/\varepsilon_m) \times 100 \qquad (2)$$

2.5.2. *Strain recovery rate (R_r)*

The temporary shape were then placed in water bath at 80°C for 5 min to recover its permanent shape. The dimension of temporary shape and shrunk (permanent shape) samples were determined at 0.1 mm accuracy using a Vernier Caliper. The strain recovery rate (R_r) quantifies the ability of the material to recover its permanent shape and is defined as follows:

$$R_f = (L_t - L_p)/(L_t - L_o) \times 100 \qquad (3)$$

Where L_o, L_s, L_t, and L_p are lengths of original, stretched, temporary (length after cooling and stress release) and permanent samples.

3 Results and Discussion

3.1 Mechanical Properties

3.1.1. *Stress strain behavior of HSR/SBR blends*

Stress strain test is the most popular and widely used over all the mechanical tests. A stress strain test not only gives the modulus and indication of the strength of the materials, but also its toughness. However, this test can be more difficult to interpret than any other test because the stress can become nonhomogenous.

Figure 1 is a representative stress-strain curve for unirradiated HSR and HSR/SBR blends with different SBR ratios namely 25, 100, 150 and 200 phr. It can be seen that the HSR sample shows yielding phenomena which is the result of crazing or breaking up the rigid continuous
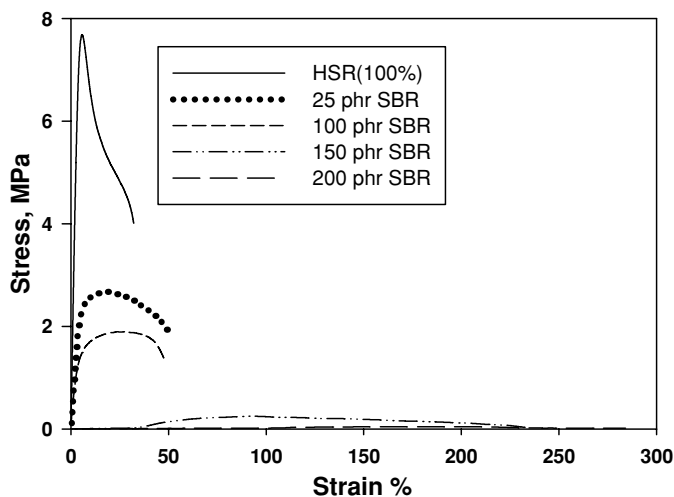
Fig. 1. Stress-strain curves for unirradiated HSR and HSR/SBR blends.

Fig. 2. Effect of irradiation dose on the tensile strength to HSR and HSR/SBR blends.

polystyrene phase (17). On the other hand, the HSR/SBR blends up to 100 phr showed broadening in yielding point with extended elongation. Also, it can be observed that HSR/SBR blends with SBR contents higher than 100 phr behave as rubbery material with uniform elongation. The stress-strain curves for HSR irradiated at doses higher than 50 kGy shows cold drawing; its length is connected with the magnitude of irradiation dose, meaning that it increases with increasing irradiation dose. The cold drawing explained by Lloyed (18) as the results of broken chains were quickly relaxed. This relaxation of stress at points of stress concentration may favor cold drawing. On the other hand, the irradiated HSR/SBR blends does not show yielding point.

3.2 Tensile Strength at Break

Figure 2 illustrates the relation between tensile strength at break and irradiation dose for HSR and its blends with SBR. It can be seen that the significant increase in the stress values at break for HSR and HSR/SBR blend was at doses higher than 50 kGy. The increase in TS continues up to 150 kGy for HSR, 25 phr and 100 phr SBR, whereas it leveled off or slightly decreased at 150 for 150 and 200 phr SBR samples. Also, it is noticed that rich styrene content samples have higher tensile strength at any irradiation doses. The tensile strength values depend on both styrene content and crosslinking density; the extent of crosslinking is dependant on the ratio of SBR component in the blend. Rich butadiene blend ratio is more susceptible to crosslinking compared to high styrene blend samples. On the other hand, polystyrene is known as a radiation resistant polymer due to the resonance stabilization of benzene ring which dissipates the energy of radiation. Therefore, high styrene content blends have low crosslinking density. The observed
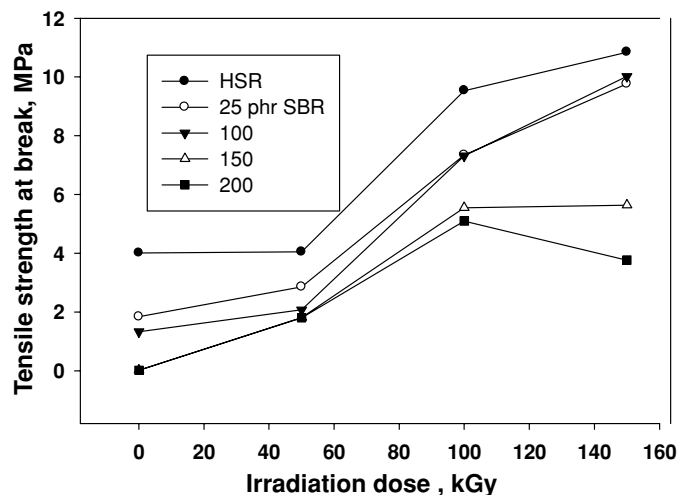
decrease in stress at break value may be attributed to the degradation reactions which takes place at high irradiation doses.

3.3 Tensile Stress at a Given Elongation ($TS_{25\%}$)

The tensile strength at a given elongation (Equation 1) is substantially proportional to the molecular weight between crosslink (Mc). Mc values represent the effective crosslinking i.e., both physical crosslinks (entanglements and hard styrene segments) and chemical crosslinks (bonds between macromolecular chains. Since the crosslinking mainly occurred between the butadiene segments chains and, to a lesser extent, in the polystyrene blocks, it is better to represent the effect of irradiation dose on the crosslinking density in terms of normalized tensile strength at 25% ($NTS_{25\%}$) not $TS_{25\%}$. $NTS_{25\%}$ is the ratio of $TS_{25\%}$ at a specific dose to that $TS_{25\%}$of unirradiated sample. From Table 1, it can be seen that the crosslinking density values increased with increasing irradiation dose and polybutadiene contents.

Table 1. Normalized tensile strength at 25% elongation for HSR and HSR/SBR blends.

Dose, kGy	HSR (100%)	25 phr SBR	100 phr SBR	150 phr SBR	200 phr SBR
unirradiated	1.00	1.00	1.00	1.00	1.00
50.00	1.10	1.20	1.06	2.71	6.60
100.00	1.91	1.98	2.39	11.46	44.80
150.00	1.83	2.23	2.98	6.67	22.40
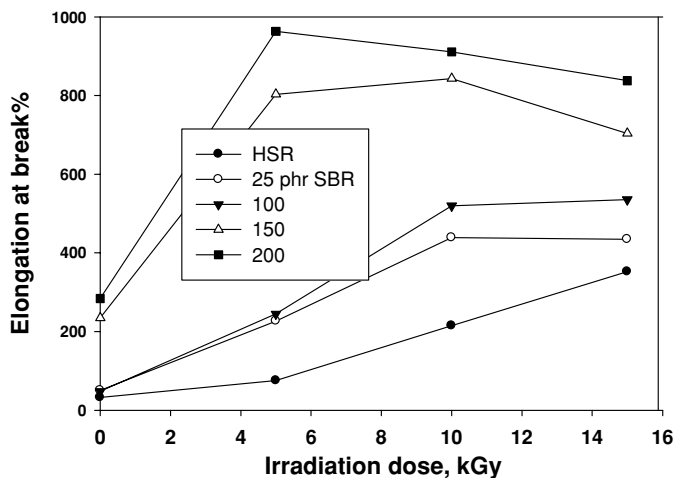
Fig. 3. Effect of electron beam irradiation dose on the elongation of HSR and HSR/SBR blends.

Fig. 4. The relation between irradiation dose and toughness for HSR and HSR/SBR blends.

3.4 Elongation to Break Point

Figure 3 shows the relation between elongation to break point (E_b) and irradiation dose for HSR and HSR/SBR blends of different ratios. It can be observed that the increase of irradiation dose is accompanied by an increase in E_b values for HSR, whereas, for 25 and 100 phr SBR blend, it tends to level off from 100 to 150 kGy. On the other hand, the E_b of the blend containing 150 and 200 phr SBR decreases beyond 50 kGy. It is apparent that the behavior of E_b with dose is largely related to the blend composition, in which the increase of SBR ratio is accompanied with decreasing the irradiation dose at which the maximum E_b value can be obtained. This means that the E_b process is dependent on the crosslinking density and there is a critical crosslinking density beyond it E_b values which begins to decline. The increased E_b observed at low doses was attributed primarily to the motion of dangling branched structure of the rubber segment incompletely attached to the network through slippage of trapped entanglement (19). Similar large elongations were observed in networks containing a substantial proportion of unattached macromolecules which are highly entangled but free to reptate (20). Buncknal and Koiwa (21, 22) reported that crosslinking to a moderate degree allows the rubber to reach high strain by fibrillation , and at the same time confers mechanical strength upon the fibrils. More recently, such phenomena was observed in SBR cured using electron beam irradiation in the presence of polyfunctional monomers (23).

3.5 Toughness

Toughness is an indication of the energy that the materials can absorb before breaking.

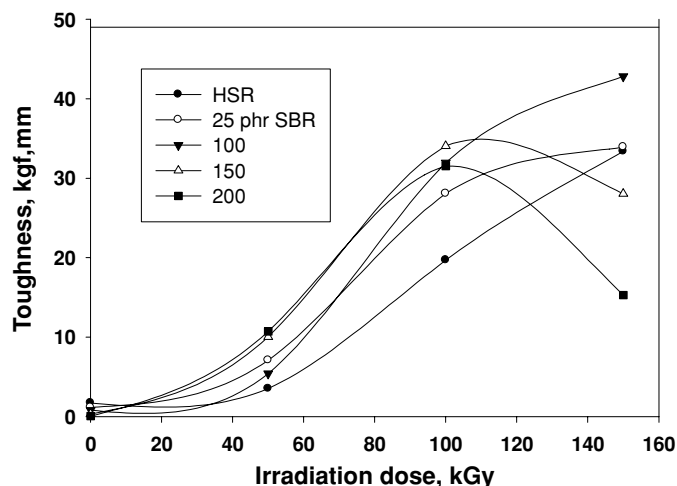Figure 4 shows the toughness as a function of irradiation dose for HSR and HSR/SBR blends with different

ratios. It can be seen that toughness increases with increasing irradiation dose for all the samples up to a dose of 100 kGy. However, blends containing 150 and 200 phr SBR showed a toughness decline at 150 kGy, which may be attributed to the occurrence of degradation at high doses. The degradation leads to catastrophic bond rupture which results in cracks leading to specimen failure at low elongation and stress. On the other hand, Cigna (24) described the sources of embrittlement for chemically crosslinked HIPS. Also, Ramsteiner (25) stated that avoiding too much crosslinking or adding oil into rubber particles increases toughness. Usually, the increase in toughness for hard HSR by incorporating rubber phase is accompanied by a decrease in other mechanical properties e.g., TS or hardness. However, it is noticed that irradiation of HSR improves its toughness without sacrificing the other mechanical properties.

3.6 Hardness

As the degree of crosslinking increases, the hardness similar to the tensile stress at a given elongation is expected to progressively increase. The tensile stress at a given elongation is measured by the force required to produce a definite elongation. A constant deformation is also produced when the hardness is measured; a needle is used for this purpose and the force required to produce the deformation is indicated by spring balance. The hardness in shore A is plotted against irradiation dose for HSR/SBR blends as shown in Figure 5. It was noticed that the hardness of HSR is higher than the scale of shore A and was not included in the figure. The figure illustrates that shore A values decrease considerably as the SBR ratio increases (150 and 200 phr SBR). On the other hand, the influence of irradiation dose is pronounced for the 150 and 200 phr SBR blends, in which a noticeable increase in shore A with increasing dose was
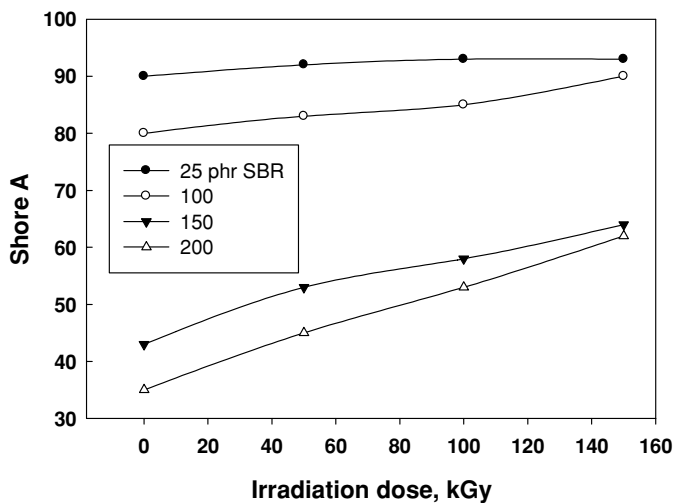
Fig. 5. Effect of irradiation dose on the harness of HSR and HSR/SBR blends.

observed. Also, it can be observed that low SBR blends ratios (25 and 100 phr SBR) are slightly affected by irradiation dose.

3.7 Shape Memory Characteristics

3.7.1. *Strain fixation rate (R_f)*

The strain fixation rate (R_f) describes exactly how the sample can be fixed in the stretched shape after deformation. The resulting temporary shape always differs from the shape achieved by deformation. Figure 6 (a, b, and c) shows the relation between irradiation doses and strain fixation rate (R_f) for HSR and HSR/SBR(100/100) and HSR/SBR(100/150) blends, respectively stretched at different temperatures. It is obvious that the increase of temperature resulted in an increase of R_f values for all the stretched specimens under investigation, therefore, high temperature is favored in order to avoid irreversible bond breakage.

Heating HSR or HSR/SBR blends near or above the heat distortion temperature (HDT) of HSR permits the hard segments of HSR (polystyrene) to easily stretch and align together. After cooling, the temporary shape is fixed as results of vitrification of polystyrene segments. High temperature stretching make hard styrene segment highly stretched; therefore more oriented. On cooling, it prevents the elastic chain recovery and as a result, R_f increased compared to low temperature stretching.

Also, it can be seen that R_f was decreased as the styrene segment decreased due to the fact that the percentage of styrene segments is not capable to fix the temporary shape as well as the fact that the increase in crosslinked butadiene increase the elastic recovery. From Fig 6(A), it can be seen that increasing irradiation dose up to 50 kGy causes a steep decrease of R_f values, whereas beyond this
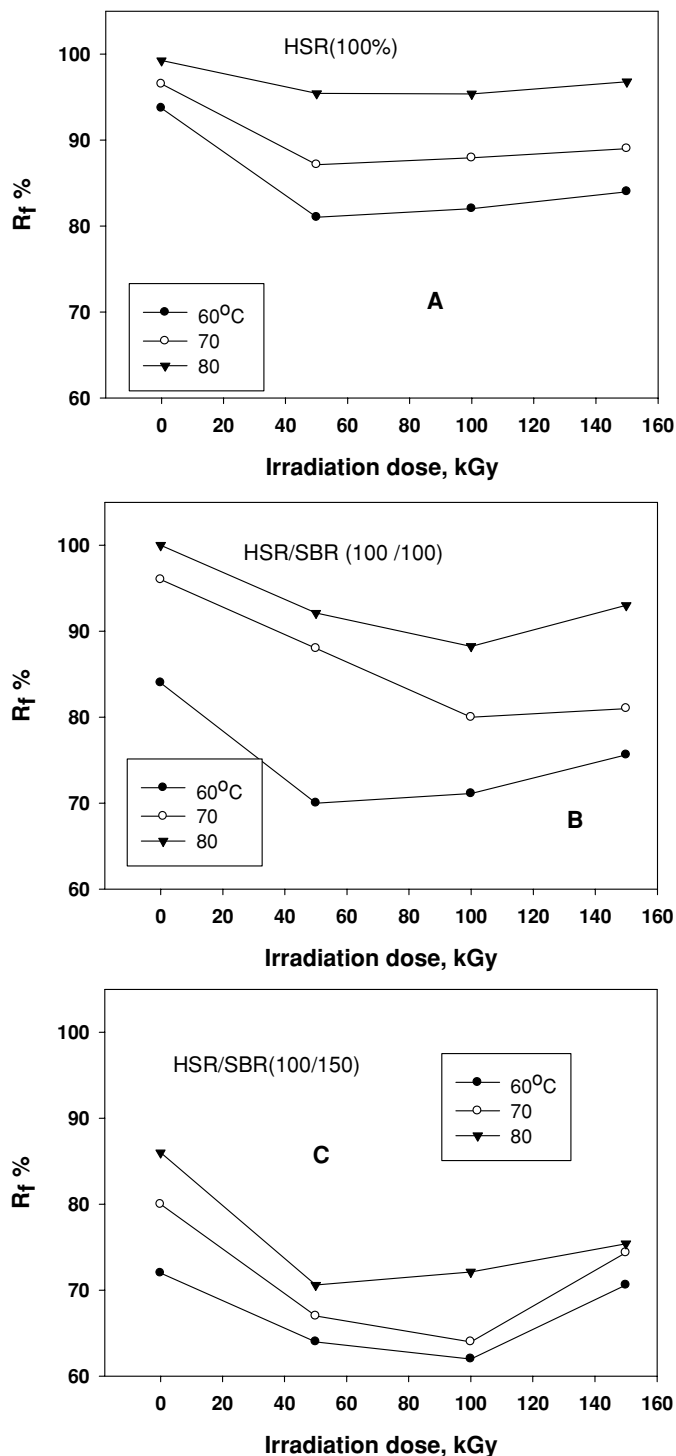

Fig. 6. Relations between irradiation dose and strain fixation rate R_f for HSR and HSR/SBR blends stretched at different temperatures.

dose, R_f tends to level off. On the other hand, the R_f of 100 and 150 phr SBR blends (Fig. 6A and B) showed a high dose dependency compared to HSR, in which the decrease in R_f continues up to 100 kGy followed by a slight increase at 150 kGy. This means that rich butadiene

segment blends are more influenced than the blends which contain high styrene segments. This may be explained based on the fact that crosslinking that takes place when the specimens are subjected to irradiations, which in turn increases its elasticity. The increase in elasticity enhances chain rebound, hence, after cooling and stabilization, the length of stretched specimens becomes shorter than the unirradiated one. The increase in R_f value at 150 kGy may be attributed to the degradation that becomes more predominant compared to crosslinking at high irradiation doses. In this case, it is difficult for chains to restore its previous shape and as a result, the length of stretched specimens after cooling stabilization is higher than the non-degraded one. The increase in elasticity was previously reported when polyethylene vinylacetate (EVA) was blended with polyethylene (PE) (26). It was found that the stretched length was decreased as the irradiation dose or EVA percent was increased.

3.7.2. *Strain recovery rate (R_r)*

The strain recovery rate (R_r) quantifies the ability of the material to recover its permanent shape In this section the temporary shaped samples, after stretching and stabilization for 24 h, are subjected to heating at 80°C to recover its permanent shape. Figure 7 (a, b and c) shows the relation between irradiation doses and strain recovery rate (R_r) for HSR HSR/SBR(100/100) and HSR/SBR(100/150) blends, respectively that previously stretched at different temperatures then reheated were at 80°C. From the figure, it is obvious that the samples previously stretched at high temperature have a high R_r value; its magnitude depends on both blend ratios and irradiation dose. Figure 7A shows that there is an abrupt increase in R_r for HSR at 50 kGy, after that, the increment in R_r was insignificant. On the other hand, the blends containing 100 and 150 SBR (Fig. 7, B and C) show a different manner in which the increase in R_r proceeds almost linearly with increasing irradiation dose. This behavior is connected with the systematic increase in crosslinking density as the irradiation dose or butadiene segments increases. Also, it can be seen that the influence of increasing temperature was higher on 100 and 150 phr SBR blends compared to HSR samples; the variation in R_r increases as the soft butadiene segment percent increased.

From the results obtained, one may observe that, both R_f and R_r parameters are influenced by the physical net point (styrene segments) and the covalent bonds generated between butadiene segments as a result of irradiation. However, during cooling of the temporary shape, the presence of covalent bonds counteract the role played by the physical net point (vitrification of styrene segment) in which the later tends to maintain fixed temporary shape, whereas the covalent bonds increase the elasticity of butadiene units leading to rebound of the stretched specimen. Consequently, R_f was negatively af-
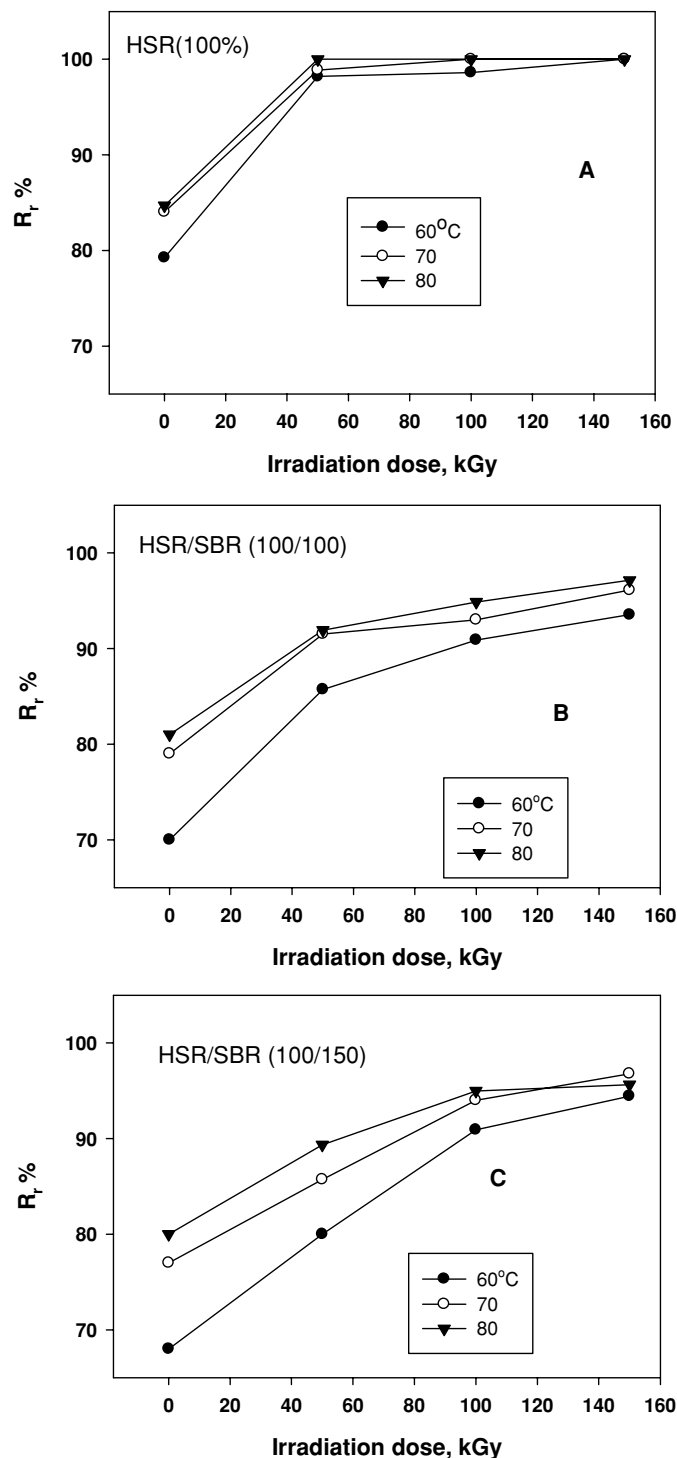

Fig. 7. Relations between irradiation dose and strain recovery rate (R_r) for HSR and HSR/SBR blends stretched at different temperatures.

fected by increasing the butadiene segment and irradiation dose. On the other hand, both covalent bonds and physical bond (styrene segments) have a synergistic effect on R_r in which both forces work in line to recover the permanent shape.

4 Conclusions

From the results obtained, one may conclude that:

A combination of both physical netpoints and chemical covalent bonds greatly enhance the mechanical properties of the specimens under investigation.

Irradiation of HSR improves the toughness without sacrificing the other mechanical properties.

The strain fixation rate R_f of HSR and HSR/SBR blends was found to be negatively influenced by irradiation, however, high styrene blend ratio was slightly affected. Conversely, R_r was improved remarkably due to increasing the irradiation dose or styrene content. Also, it was observed that increasing the stretching temperature increases both R_f and R_r.

In spite of the decrease in R_f values due to irradiation, the presence of covalent bonds is necessary for the long period's storage of the temporary shape esspecially in applications like heat shrinkable materials. The covalent bonds prevent relaxation and reorganization of the polymeric; as a result, the dimensional stability of the permanent shape improved.

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