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# Radiation Vulcanization of Nitrile Butadiene Rubber/Butadiene Rubber Blends

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Blends of nitrile butadiene rubber (NBR) with butadiene rubber (BR) with varying ratios have been prepared. Vulcanization of prepared blends has been induced by ionizing radiation of gamma rays with varying dose up to 250 kGy. Physical properties, namely soluble fraction and swelling number have been followed up using toluene as a solvent. Mechanical properties, namely tensile strength, tensile modulus at 100% elongation and elongation at break have been followed up as a function of irradiation dose, as well as blend composition. Thermal stability of blends was studied by TGA. The result indicated that the addition of NBR has improved the properties of NBR/BR blends. Also, NBR/BR blend is thermally stable than BR alone.

**Keywords:** gamma radiation; nitrile butadiene rubber; butadiene rubber; blends



## 1 Introduction

Blending of polymers has gained much interest in the last three to four decades, due to the fact that it can be used to produce new polymeric materials, i.e., compositions with specific properties suitable for certain special application.

Elastomeric blends are known for a long time and are technologically important materials due to their several applications. Their chemical and physical properties make them suitable as engineering materials, for chemical industry, electric insulators and many other uses (1–5).

Radiation vulcanization of rubber is one of the most promising tools for obtaining a valuable product with reasonable physico-mechanical properties without any need for adding different ingredients usually used in conventional vulcanization methods.

Blends of nitrile butadiene rubber (NBR), with ethylene propylene diene monomer (EPDM), have been vulcanized by gamma irradiation. The results indicated improvements in mechanical properties with increasing irradiation dose and NBR content in the blend (6).

The effect of radiation dose on the mechanical properties of natural rubber (NR) with butadiene rubber (BR) was studied. The results show that the mechanical properties, especially tensile strength, elongation at break and tear strength have been improved by radiation vulcanization (7).

Polybutadiene rubbers are usually blended with NR or SBR and find their largest application in the tire industry. They can impart improved abrasion resistance, resilience, low temperature flexibility, and increased groove cracking resistance (8). Moreover, compatibility improvement of NR/EPDM blends by introducing a third polymer such as BR, SBR or exposure to gamma radiation to create crosslinks between the rubber chains was studied (9). To reduce the cost and improve the mechanical properties of NR/BR blends, studies have been carried out using different methods (10, 11).

The effect of radiation dose on the mechanical properties of NR/BR blends was studied. The results obtained by the authors (12) showed that the mechanical properties have been improved significantly by radiation vulcanization. Blends of NR/NBR are noted for its oil resistance (13).

The present study is a part of systematic work carried out to explore the effects of gamma radiation on blends containing different types of elastomers. Thus, degradable polymers such as butyl rubber has been blended with crosslinkable rubber such as NBR, while in this work, both the components NBR and BR are crosslinkable under the effects of gamma irradiation. Thus, blends of NBR and BR in different ratios of BR and NBR were prepared and subjected to gamma irradiation at different radiation doses and compared with each one of the components alone. The results obtained are given to show both effects of blend ratios and radiation

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doses on the physico-chemical, mechanical and thermal behavior of the blends.

## 2 Experimental

### *2.1 Materials*

Nitrile-butadiene rubber with the commercial name KRYNAC 4050 was supplied by Bayer, Leverkusen, Germany. It is characterized by having an average acrylonitrile content of 40% by weight, Mooney viscosity $ML_{1+4}$ (100°C) $50 \pm 5$ and density 0.98 ($g/cm^3$). Butadiene rubber was supplied by Dow Chemical Co., USA. Its cis-1,4 content is 97%, Mooney viscosity, $ML_{1+4}$ is 48. The recipe in this study contained the rubber components in different ratios and also other additives, namely: ZnO, 5 phr; stearic acid, 1.0 phr and dibutylphthalate (DBP), 5 phr.

### *2.2 Preparation of Blends*

Ingredients of the recipe were mixed carefully through a two roller mill, 300 dia. × 470 mm in length, with a gear ratio of 1.14:1 at 80°C to obtain sheets, which are pressed to 1 mm thickness using a hot electric press at 150°C for 20 min at a pressure of 16 MPa. Irradiation by gamma cell type 4000 A from India at a dose rate of 7.6 kGy/hr, was carried out.

### *2.3 Measurements*

Soluble fraction (SF) expressed as the fraction of soluble weight, was obtained by extracting the soluble part in solvent using Soxhlet for 24 h and drying the insoluble part completely in vacuum at 50°C. The swelling number (SN), on the other hand, was determined after allowing an accurate weight of sample to swell for 24 h in solvent. The solvent used for both parameters was toluene.

The mechanical properties, namely tensile strength (TS), tensile modulus at 100% elongation ($M_{100}$) and elongation at break percentage ($E_b$) were carried out using a universal testing machine of the INSTRON model 1195, England. The given results are the mean value of three separate specimens. The error in these measurements is 5%.

Thermal analysis was carried out using thermal gravimetric analysis (TGA) apparatus, whereby samples of (0.98–1.5 mg) were encapsulated in aluminum pans and heated from 50 up to 600°C at a heating rate of 10°C/min under nitrogen atmosphere.

## 3 Results and Discussion

### *3.1 Physical Properties*

The physical properties that have been followed up in the present study are the soluble fraction % (SF), and the swelling number SN. Toluene as a solvent has been used for conducting these measurements. The solubility parameter of toluene ($\rho$) is 8.9 $(cal/cc)^{1/2}$, which is nearly close to that of NBR rubber of ($\rho$) = 9.4 $(cal/cc)^{1/2}$ and that of BR rubber of ($\rho$) = 8.6 (14).

### *3.2 Soluble Fraction % (SF)*

The variation of SF as a function of irradiation dose for NBR, BR elastomers and their blend is shown in Figure 1, whereby the solvent used is toluene. It can be seen that BR vulcanizates have attained the largest values of SF over the entire range of irradiation, whereas vulcanizates of NBR have attained the smallest values. The SF values attained by blends lie also between these two extremes and they decrease systematically with increasing the content of NBR in the blend when comparing these values at the same irradiation dose. Moreover, SF values attained by different vulcanizates decrease with increasing irradiation dose; this latter behavior is of course, affiliated with an increased extent of network structure, i.e., insoluble gel due to increased radiation-induced crosslinks with increasing irradiation dose. Apparently, this latter process, i.e., network formation takes place with an increased rate in the case of NBR vulcanizates with respect to BR and mainly in the lower range of irradiation, namely between 50 kGy and 100 kGy. Moreover, the change in SF values is a limited one as it decreases from about 12% at 50 kGy to ~9% at 250 kGy for NBR rubber vulcanized.

This data given above clearly indicates that the extent of the insoluble part in any vulcanizate increases with increasing the irradiation dose, as well as the NBR content. This insoluble part, however, is composed of an insoluble network structure, as well as an insoluble uncrosslinked part of the elastomer. Contribution to both parts from NBR is higher, which would account for the obtained results.

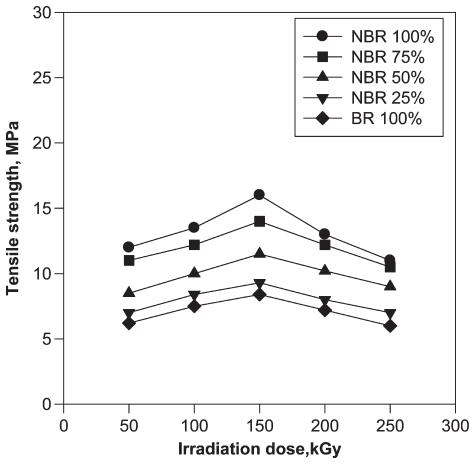


**Fig. 1.** Effect of irradiation dose on tensile strength of NBR < BR, and NBR/BR blends.

### *3.3 Swelling Number (SN)*

The results obtained for the variation of SN, for unloaded NBR, BR and their blends in toluene as solvent, as a function of dose of irradiation are shown in Figure 2. It may be seen that BR has attained the largest values of SN over the whole range of irradiation whereas NBR has attained the smallest values. The blends have attained values that lie between these two extremes. Moreover, it may be observed that the value of SN of different rubber compositions decreases with increasing the radiation dose and with increasing the NBR content in the blend. The first observation may be correlated with increased extent of crosslinking with increased irradiation dose. On the other hand, the second observation as well as the attainment of NBR vulcanizates of lower SN with respect to the ones attained by BR may be correlated firstly with the increased rate of crosslinking of NBR with respect to BR and secondly with its decreased rate of solubility in toluene with respect to BR.

### *3.4 Mechanical Properties*

The mechanical-properties that have been followed up in the present investigation are the tensile strength, tensile modulus at 100% elongation and the elongation at break. These properties were followed up firstly for the gum rubbers and then their blends as a function of irradiation dose, as well as the concentration % of NBR in the blend.

### *3.5 Tensile Strength TS*

Figure 3 shows the variation of TS values for the induced radiation vulcanization of both NBR and BR gum rubbers, as well as their blends. It can be seen that the TS values for all compositions increase with increasing the irradiation dose reaching its maximum value at 150 kGy and then decreases for doses higher than that. It may also be observed that NBR vulcanizates have attained the highest TS values over the entire range of irradiation, whereas BR vulcanizates have attained the lowest values. The TS values attained by blend vulcanizates lie between these two extremes and decreases systematically with increasing BR content in the blend. Moreover, it may be observed that the TS values attained by the NBR vulcanizates are almost double as much as that attained by BR vulcanizates, when the TS values are compared at the same irradiation dose.

On irradiation of polymeric materials, such as rubber for example, both radiation induced crosslinking and degradation processes take place simultaneously but with different rates. Accordingly, the data obtained indicate that the crosslinking process was the dominating one for doses up to150 kGy whereas the degradation process has apparently prevailed for doses higher than 150 kGy. One cannot, however, exclude the impairment of chain orientation of rubber macromolecules due to increased extent of induced crosslinking at higher dose and hence its eventual contribution in decreasing the TS values for doses higher than 150 kGy.

NBR is known to be a totally amorphous rubber and is considered as polar rubber due to the presence of CN groups of the polyacrylonitrile content of the rubber. Self-reinforcement due to crystallization expected at high elongation of NBR elastomer would not take place whereas contribution, affiliated with dipole-dipole attraction to TS values may be expected.

Its magnitude however, is a limited one as acrylonitrile constitutes only about 40% of the rubber. Hence, it may be concluded that it is not the main factor affecting the obtained TS values. BR on the other hand, is characterized by its regular structure and the high cis-1,4 content of 97% that is used in the present studys is known to crystallize at room temperature when stretched over 200% (15). Therefore, it would be expected that some contribution to TS property may take place in addition to that affiliated with radiation induced crosslinking. The results obtained clearly indicate that TS values of NBR are almost twice that of BR. This

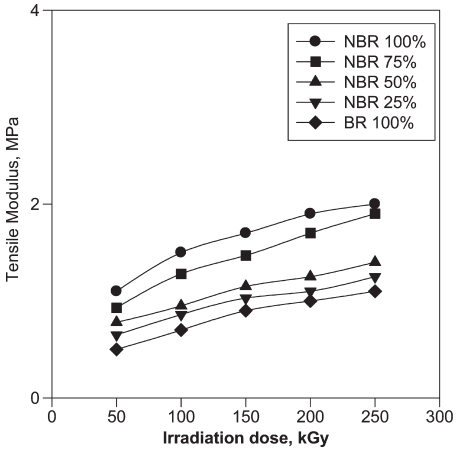


**Fig. 2.** Effect of irradiation dose on modulus of NBR, BR and NBR/BR blends.

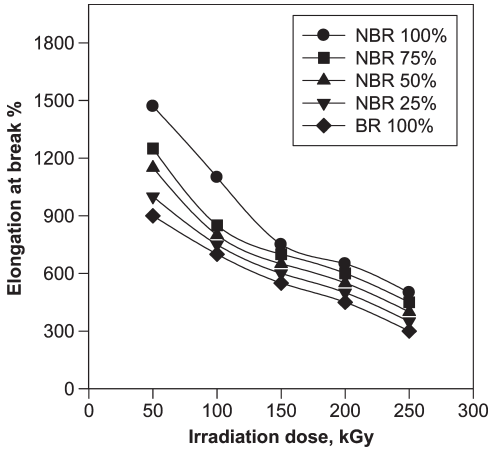


**Fig. 3.** Effect of irradiation dose on elongation at break % of NBR, BR, and NBR/BR blends.

behavior is mainly affiliated again with the molecular structure of the two rubbers, which are both considered as radiation crosslinkable rubbers. Consequently, the magnitude of free radicals formed by irradiation, their reactivity and participation in crosslink formation ought to be higher in NBR than in Br.

### *3.6 Tensile Modulus, $M_{10}$*

Figure 4 illustrates the variation of $M_{100}$ as a function of irradiation dose for gum NBR, gum BR and their blends. It can be seen that the $M_{100}$ of all samples increases in a semi-linear manner with increasing the irradiation dose, whereby the NBR elastomer has attained the highest value and BR rubber, the lowest one. The value attained by the NBR/BR blend lies in between and it decreases systematically with increasing the concentration % of BR in the blend. Moreover, and contrary to attained TS values, the $M_{100}$ values attained by all compositions are relatively small ones and its range of variation with increasing the irradiation dose is a limited one. These data indicate that NBR vulcanizates has attained the relatively highest retractive force, i.e., resistance to strain deformation or stretching. On the other hand, NBR/BR blends has attained values in between that of NBR and BR.

This behavior is affiliated with the highly entanglement occurrence and coiled-up nature of NBR, which would not undergo much change on stretching due to induced crosslinking of considerable extent as previously mentioned. BR, on the other hand, is of regular structure and the extent of radiation crosslinking is a limited one, which allows for extending on being stressed. Moreover, the contribution to $M_{100}$ from crystallization of BR at 100% elongation is apparently a limited one. The systematic increase in the value of $M_{100}$ of the blend with increasing the content of NBR is attributed, as is known to the additive nature of the tensile modulus property.

In this respect, the tensile modulus of a system of more than one component is proportional to the sum of the modulus of each component multiplied by its weight or volume fraction (16), as shown in Table 1.

The latter, additively and hence, proportionally behavior can be seen from the depicted values of $M_{100}$ as a function of NBR content in the blend as seen in Figure 5. A linear behavior has been attained over the entire range of NBR concentration higher than 50 wt% of the blends.

This positive deviation indicates that a contribution to the value of $M_{100}$ by the value of NBR is more effective at a high degree of irradiation and high concentration.

### *3.7 Elongation at Break, $E_b$*

Variation of $E_b$% as a function of irradiation dose for gum NBR, gum BR and their blends, is illustrated in Figure 6. It can be seen that the value of $E_b$ for all samples decreases with increasing the irradiation dose. Moreover, gum NBR vulcanizates has attained the largest $E_b$% value over the entire range of irradiation, whereas gum BR vulcanizates has attained the lowest values. The values attained by blends lie between these two extremes and their values increase with increasing the content of NBR in the blend.

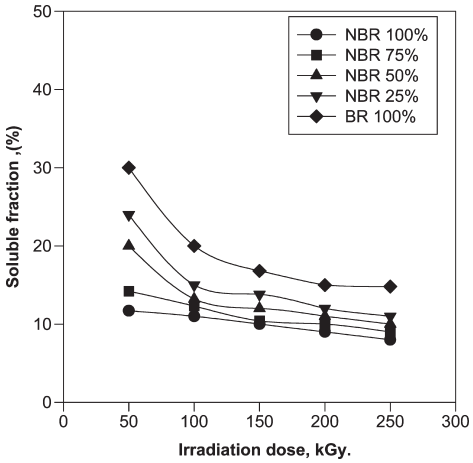


**Fig. 4.** Effect of irradiation dose on soluble fraction % of NBR, BR, and NBR/BR blends (in toluene).

The results obtained are not the expected ones with respect to those of TS measurements given before in Figure 3, as it would have been expected that the $E_b$ values of BR to be higher than those attained by NBR when taking the extent of induced crosslinking into consideration. Knowing, however, that the difference in magnitude of crosslinking of the two rubbers is a limited one, and then the difference in $E_b$ values is affiliated mainly with the structure of the rubber. NBR is known to be a totally amorphous rubber having a bulky nitrile groups and hence, its totally coiled-up structure with its considerably large physical entanglements would be expected to be effective in counteracting

**Table 1.** Calculated and experimental tensile modulus values of NBR/BR blends at different irradiation dose

| Dose, kGy | Blend ratio, NBR/BR | Calculated values | Experimental values |
|---|---|---|---|
| 50 | 75/25 | 0.95 | 0.93 |
| | 50/50 | 0.8 | 0.78 |
| | 25/75 | 0.65 | 0.65 |
| 100 | 75/25 | 1.3 | 1.2 |
| | 50/50 | 1.1 | 0.95 |
| | 25/75 | 0.9 | 0.86 |
| 150 | 75/25 | 1.5 | 1.47 |
| | 5050 | 1.3 | 1.15 |
| | 2575 | 1.1 | 1.03 |
| 200 | 75/25 | 1.7 | 1.7 |
| | 50/50 | 1.45 | 1.25 |
| | 25/75 | 1.23 | 1.1 |
| 250 | 75/25 | 1.7 | 1.9 |
| | 50/50 | 1.55 | 1.4 |
| | 25/75 | 1.33 | 1.25 |

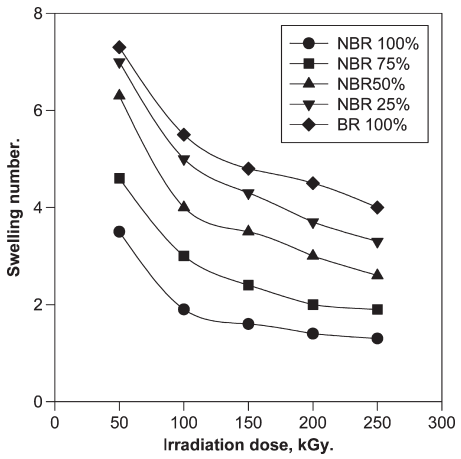


**Fig. 5.** Effect of irradiation dose on selling number of NBR, BR, and NBR/BR blends (in toluene).

the effect of induced crosslinking and hence, higher $E_b$ values for NBR gum vulcanizates are expected. On the other hand, BR rubber, as mentioned before, is regularly ordered and may undergo crystallization on large stretching. Hence, it would be expected that this kind of structure would contribute effectively in reducing the value of $E_b$ attained by BR vulcanizates, despite its limited extent of crosslinking with respect to NBR vulcanizates. Accordingly, increasing the content of BR in the blend would result in decreasing its $E_b$ value, which is the case experimentally.

### *3.8 Application of Flory-Rehner Equation*

Application of the Flory-Rehner equation yields the number of active network chain segments per unit volume, as a measure of extent of vulcanization. The variation of number of active chains per unit volume (mole/cm$^3$) as a function of irradiation dose for NBR, BR and their blends is shown in Figure 7. It can be seen that the values of number of active chains per unit volume, (n) for NBR and NBR/BR of high content of NBR i.e. 75 phr increase with increasing irradiation dose up to 200 kGy and then decreased. On the other hand, for NBR/BR blends having 50, 25, 0 phr of NBR the (n) values slightly increase with increasing irradiation dose. Moreover, it may be observed that the values of (n) generally increase with increasing the NBR content in the blend at any certain irradiation dose. These values have been calculated according to Equation (1) (Flory-Rehner equation) (17).

$$[\ln(1 - V_r) + V_r + \mu V_r]n = V_1(V_r^{1/3} - V_r/2) \qquad (1)$$

Where, n is the number of active chains segments per unit volume; $V_r$ is the volume fraction of polymer in swollen mass; $V_1$ is the molar volume of solvent; $\mu$ is the Flory-Huggins polymer–solvent interaction.

The value of (n) has been taken as an index of the level of crosslinking of NBR, BR and their blends induced by gamma irradiation. Hence, it may be said that the crosslink density increases with increasing the NBR content in the blend as well as gamma irradiation dose (18). The data given in this figure offer further confirmation for results of mechanical properties that has been given before.

Figure 8 shows the Charlesby-Pinner plot of NBR, BR and NBR/BR blends irradiated with gamma rays. The Charlesby-Pinner equation is given as follows (19):

$$S + \sqrt{S} = p/q + 1/quR$$

where S is the soluble fraction; R is the radiation dose expressed in kGy; q is the proportion of units crosslinked; p is the ratio of main fractures to chain units; u is the average number of repeat units per molecule before irradiation.

From this figure it can be seen that the crosslinking process predominates during gamma irradiation. For butadiene rubber the rate of crosslinking (soluble fraction decrease) is higher than that of NBR. For blends, the rate increases with

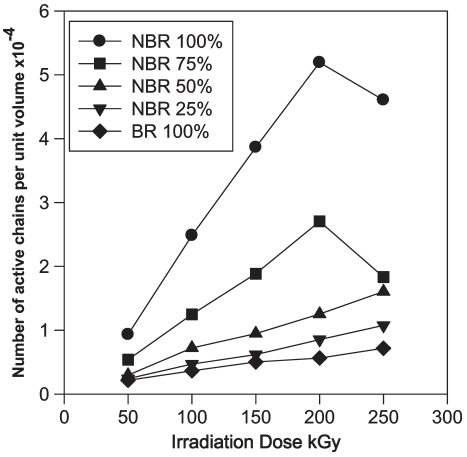


**Fig. 6.** Number of active chains per unit volume as a function of irradiation dose for NBR, BR, and NBR/BR blends.

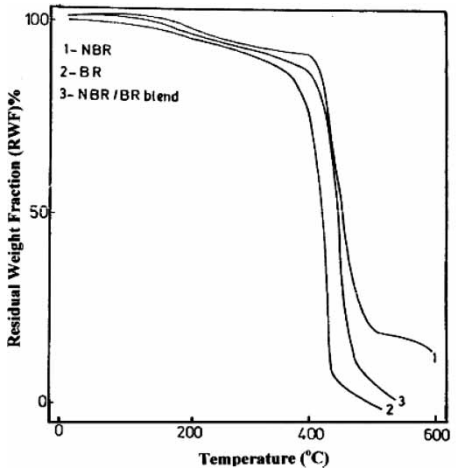


**Fig. 7.** TGA thermograms for thermal decomposition of NBR, BR, and NBR/BR blend (50/50) at dose 20 kGy.

increasing the BR content in the blend governing by the slope of the curve.

### 3.9 Thermogravemetric Analysis (TGA)

Figure 9 shows illustrative thermograms for NBR, BR, and NBR/BR (50/50) blend irradiated at a dose of 200 kGy.

These thermograms show the variation of residual weight fraction % (RWF%), as a measure of weight loss of samples, and as a function of heating temperature. It may be observed that the RWF% value for NBR has experienced a limited weight loss of ~8% in the temperature range from 150°C to ~410°C, which may be attributed to decomposition of impurities as well as additives. On raising the temperature higher than 410°C, the RWF% value encountered a rapid drop in its value reaching ~16% at 600°C. Also, it can be seen that for the thermogram corresponding to BR, the RWF% value has experienced weight loss of ~11% in the temperature range from 100°C to ~380°C. On raising the temperature, the RWF% value undergoes a rapid drop again and reaches almost 2% at 500°C. On the other hand, it can be seen that for the thermogram corresponding to the NBR/BR (50/50) blend, the RWF % value has experienced a weight loss of ~13% in the temperature range from 150°C to 400°C and on raising the temperature, the RWF% value shows a rapid drop and reaching almost 5% at 550°C. Moreover, it may be noticed that the starting decomposition temperature for NBR rubber is about ~417°C and for BR is about 380°C, whereas for the NBR/BR (50/50) blend, the decomposition temperature is about ~410°C. These data indicate that BR has decomposed first, then the NBR/BR blend, and finally, NBR. This means that the addition of NBR to BR improves its thermal stability i.e., the NBR/BR blend is more thermally stable than BR alone.

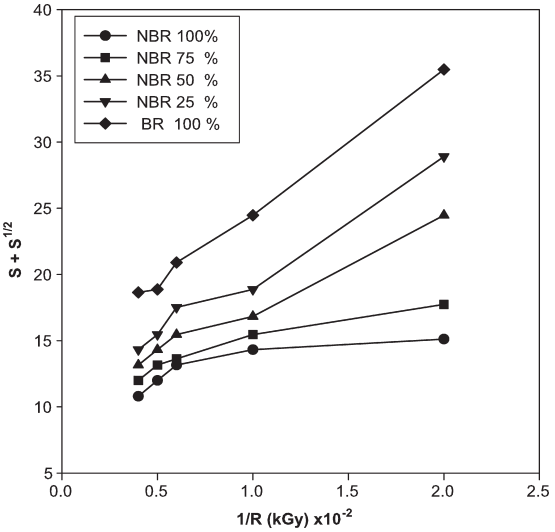


**Fig. 8.** Charlesby-Pinner plots for gamma irradiated NBR, BR, and NBR/BR blends.

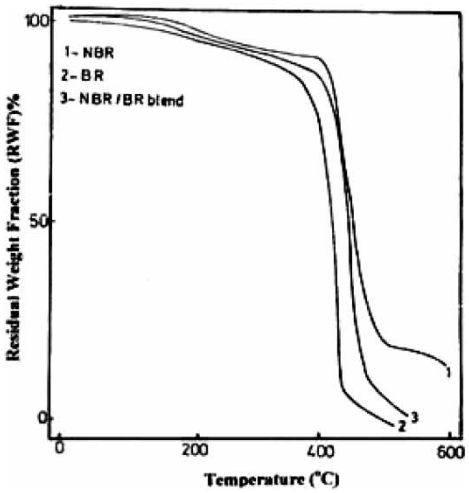


**Fig. 9.** TGA thermogram for thermal decomposition of NBR, BR, and NBR/BR blend (50/50) at dose for 200 kGy.

## 4 Conclusions

From the results obtained in the present investigation, the following conclusions may be deduced: The mechanical properties of radiation-induced gum butadiene rubber, which are effectively low, have increased positively on blending it with nitrile butadiene rubber.

The improvement attained in mechanical properties has been certified by measurements of physical properties of prepared blends. The magnitude of improvement is a function of irradiation dose, as well as the amount of nitrile butadiene rubber in the blend. Also, the thermal stability of butadiene rubber has been improved by blending it with nitrile butadiene rubber.

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