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Effect of gamma irradiation on the properties of natural rubber/styrene butadiene rubber blends

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Abstract Blends of natural rubber (NR) with styrene butadiene rubber (SBR) with varying ratios have been prepared. Vulcanization of the prepared blends has been induced by irradiation of gamma rays with varying doses up to 250 kGy. Mechanical properties, namely tensile strength, tensile modulus at 100% elongation, elongation at break have been followed up as a function of irradiation dose as well as blend composition. Physical properties, namely gel fraction and swelling number have been followed up using benzene as a solvent. Thermal measurements namely thermogravimetric analysis were carried out. The results indicated that the addition of NR has improved the properties of NR / SBR blends. Also NR/SBR blend is thermally stable than NR alone.

1. Introduction

Elastomer blends are technologically important materials in the rubber industry as they achieve the best compromise in physical properties, processability and cost.. Their chemical and physical properties recommend them as engineering materials for chemical industry, electric insulators and many other uses (Burillo et al., 2002; Zhang and Chen, 2004; Al-Malaika and Kong, 2005; Fraisse et al., 2005; Yordanov and Minkova, 2003).

Blends of NR with polybutadiene rubber BR, or styrene–butadiene rubber SBR, have improved abrasion resistance, resilience, low temperature flexibility, and increased groove cracking resistance (Montgomery, 2000; Couch and Short, 1998). Mechanical properties, thermal stability, gas permeability and phase morphology of NR/Bromobutyle rubber (BIIR) blends were studied; the results indicated that the relatively large connected structure of the dispersed BIIR can act effectively as a gas barrier and the thermal stability of the blend was improved (Rattanasom et al., 2009). Also, blends of NR/acrylonitryl-butadiene rubber, NBR are noted for their oil resistance (Sirisinha et al., 2001). Moreover, compatibility improvement of natural rubber/ethylene–propylene diene monomer EPDM, rubber blends has been achieved by introducing a third polymer, BR, SBR, or polyethylene PE (El-Sabbagh, 2003). Also, the influence of silica loading on the mechanical properties and resistance to oil and thermal aging of NR/CR blends was studied (Pongdhorn et al., 2007). The viscoelastic properties of the blends of CR with EPDM,

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BR, and NR at different temperatures were studied; the results indicated that on increasing of EPDM, BR and NR ratio in CR blends the properties were improved (Fulin et al., 2007). To reduce the cost and improve the mechanical properties of NR/BR blends, studies have been carried out using different methods including radiation vulcanization (Essawy and El-Nashar, 2004; Kim and Hamed, 2000; Van de Ven and Noordormeer, 2000). The thermal stability of NR, SBR and their blends vulcanized by sulfur (Ranimol et al., 2006) was also studied.

Natural rubber possesses good dynamic and mechanical properties. However, some of its properties, such as weathering and oil resistances are much lower than those of synthetic rubbers. Blending NR with SBR rubber is one of the ways of combining good properties of the two rubbers, modifications of processing characteristics and cost reduction of the final product. NR/ SBR blends were used widely in tire and automobile industry because of very good abrasion resistance and it is also used for the production of pipe and shoe sole (Dubey et al., 2008). Moreover, both elastomers are categorized as predominantly radiation-induced crosslinking type of polymers (Woods and Pikaov, 1994). This property is in accord with the fact that radiation vulcanization of rubbers is one of promising tools for obtaining valuable products with reasonable physico-mechanical properties without any need for adding different ingredients usually used in conventional methods (Abou Zeid et al., 2001). In the present work, a study has been carried out on radiation vulcanization of NR/SBR blending system. The mechanical, physical and thermal properties of the prepared blends were followed up.

2. Materials and methods

2.1. Materials and sample preparation

NR was supplied by DOW chemical co., USA. Its cis-1,4 content is 97%, Mooney viscosity, ML_{1+4} is 48. Commercial grade styrene–butadiene rubber of grade 1502 with 23.6 wt% of styrene content was used. The recipe of this study contained also other additives, namely: ZnO, stearic acid and tetrene. The first two additives act as accelerators as well as activators and their content was 5 wt% and 1 wt%, respectively. 1ml of tetrene, on the other hand acts as antioxidant Ingredients of the recipe were mixed carefully through a two roller mill of size 300×470 mm with a gear ratio of 1.14:1 at 80 °C to obtain sheets, which were 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/h, was carried out.

2.2. Measurements

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%.

The physical properties that have been followed up are the gel fraction and the swelling number. Gel fraction% expressed as the fraction of insoluble weight, was obtained by extracting the soluble part in benzene using soxhlet for 24 h, and drying

the insoluble part completely in a vacuum oven at 50 °C. It is given by

Gel fraction% (GF%) = $W_1/W_0 \times 100$

where W_0 = initial weight, W_1 = final weight, i.e., gel weight.- Degree of swelling in benzene for 24 h at room temperature was calculated using the following equation:

Swelling number = $W_2 - W_1/W_1$

where W_1 = gel weight, W_2 = swollen weight. The solvent used for both parameters was benzene.

Thermal stability 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. Mechanical properties

3.1.1. Tensile strength, TS

Fig. 1 shows the variation of TS values for the induced radiation vulcanization of both NR and SBR 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 decrease for doses higher than that. It may be observed also that vulcanized NR has attained the highest TS values over the whole range of irradiation, whereas vulcanized SBR has attained the lowest values. The TS values attained by vulcanized blends lie between these two extremes and decreases systematically with increasing SBR content in the blend.

On irradiation of polymeric materials such as rubbers 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 to 150 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 a higher dose and hence its eventual contribution in decreasing the TS values for doses higher than 150 kGy.

SBR in its raw form represents an amorphous and homogenous polymeric material and hence the bulk mechanical properties of the radiation-vulcanized product may be fairly anticipated on the basis of its intrinsic chemical structure and irradiation conditions. Hence, self-reinforcement dose not take place at high extensions, as in case of NR and no contribution to its tensile strength would be expected.

Based on its chemical structure, the tertiary substituted carbon atom on the main macromolecules chain represents the most susceptible carbon atoms and on irradiation breakage of this bond takes place favorably leading to the formation of the hydrogen atoms and benzyl-type radical.

The formed benzyl radical undergoes resonance stabilization with the phenyl ring of the styrene monomer. Such resonance stabilization would be expected to decrease the efficiency of the benzyl radical and at the same time increases its half-life. When it happened that such radicals stand favor-
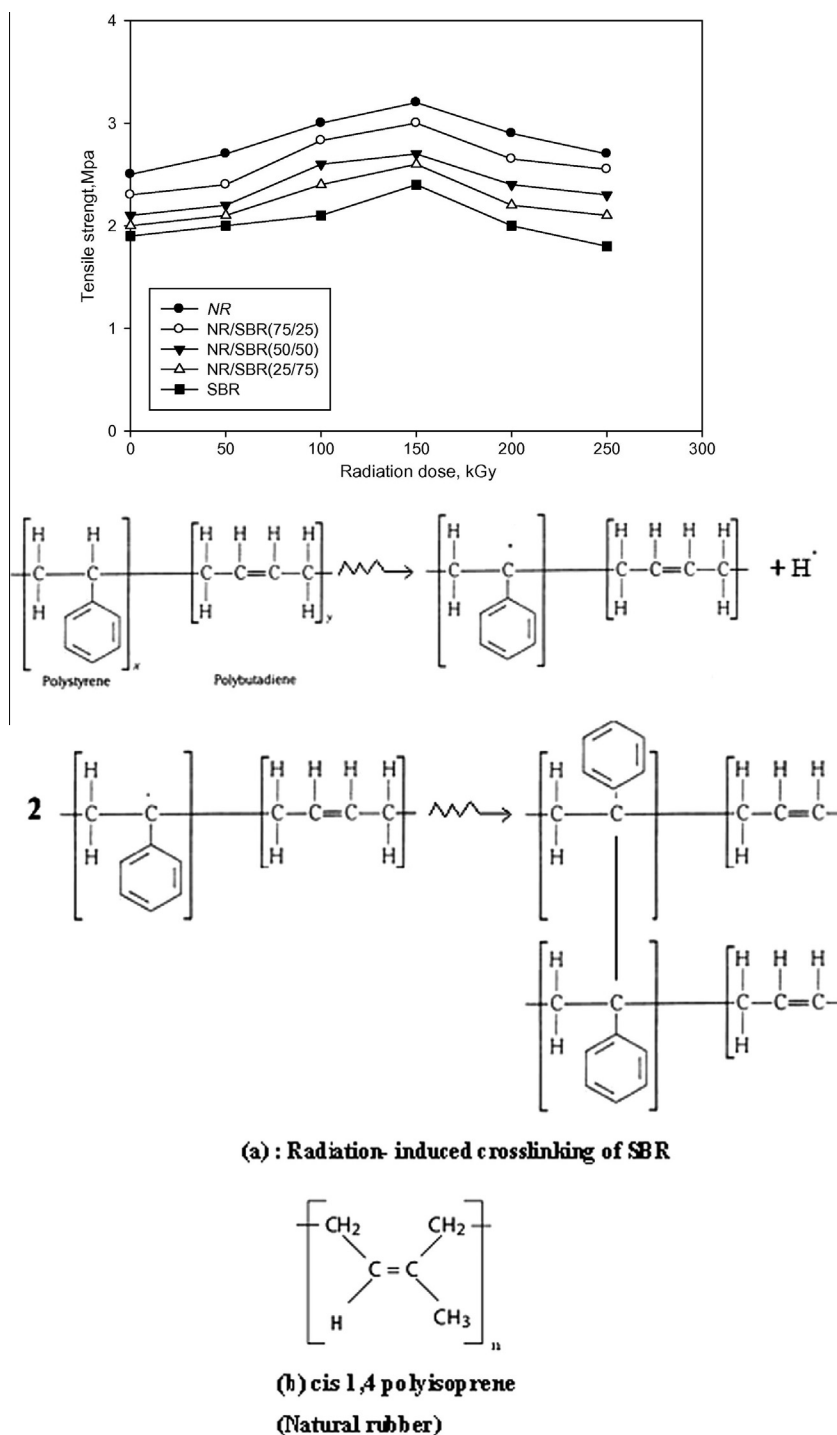
Figure 1 Effect of irradiation dose on the tensile strength of NR, SBR and NR/SBR blends. (a) Radiation induced crosslinking of SBR; (b) cis 1,4 polyisoprene (natural rubber).

ably to each other then they may react with each other with the result of formation of a covalent bond, i.e., crosslink between two adjacent macromolecules as shown in Fig. 1(a).

The formation of such a bond would be expected to be a function of the content of styrene in the copolymer, which makes 23.6 wt% as mentioned before. Under such circumstances a limited crosslinking density would be expected which

accounts for the relatively low value of TS attained by vulcanized raw SBR.

Natural rubber is also categorized as a radiation crosslinking type of polymer as it contains a double bond in its basic cis 1,4 polyisoprene unit as shown in Fig. 1(b). Moreover, it is characterized by its ability to crystaline on stretching and the absence of such groups as phenyl group in its structure as in

the case of SBR. Due to these properties, it would be expected that NR attains higher TS than SBR, which is the case.

3.1.2. Tensile modulus, M_{100}

Fig. 2 illustrates the variation of M_{100} as a function of irradiation dose for gum SBR, gum NR 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 NR elastomer has attained the highest value and SBR rubber the lowest one. The value attained by the NR/SBR blends lies in between and it decreases systematically with increasing the concentration% of SBR in the blend. These data indicate that NR vulcanizates have attained the relatively highest retractive force, i.e., resistance to strain deformation or stretching.

On the other hand, NR/SBR blends have attained values in between that of NR and SBR. Isolated double bonds in NR inhibited the formation of intra-molecular links thus resulting in the increase of the crosslinking rate, which results in a substantial increase in tensile modulus.
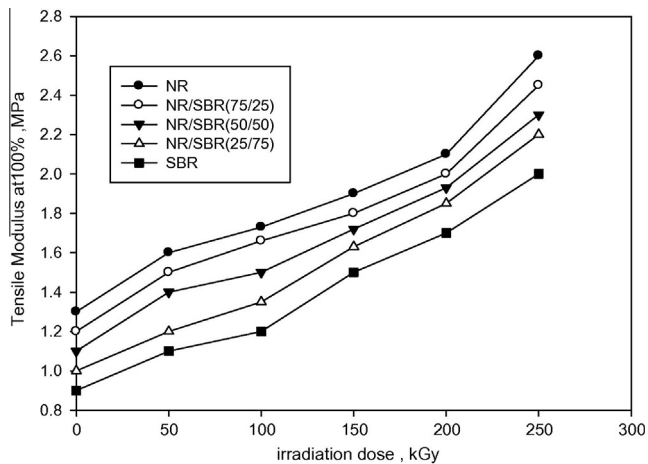

Figure 2 Effect of irradiation dose on the tensile modulus at 100% elongation (M_{100}) of NR, SBR and NR/SBR blends.
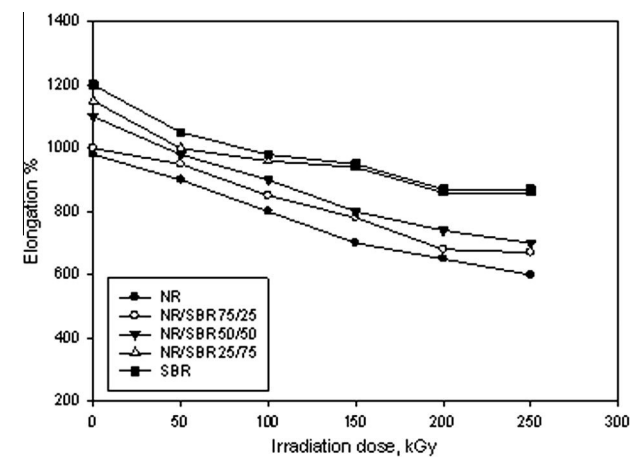
3.1.3. Elongation at break, E_b

Variation of E_b% as a function of irradiation dose for gum SBR, gum NR and their blends, is illustrated in Fig. 3. It can be seen that the value of E_b for all samples decreases with increasing the irradiation dose.

The E_b% decreases with an increase of the NR loading%. This can be attributed to the amorphous and crystalline nature of SBR and NR, respectively and this trend may be attributed to the rigid SBR/NR interface upon increasing content of NR%. This is a similar case as increasing particulate filler in the rubber compounds. It was found that the increase in filler content resulted in the reduction of the deformability of a rigid interface between the filler and rubber matrix (Wang et al., 2009).

3.2. Physical properties

3.2.1. Gel fraction% GF%

The variation of GF% as a function of the irradiation dose for NR, SBR elastomers and their blends is shown in Fig. 4, whereby the solvent used is benzene. It can be seen that NR vulcanizates have attained the largest values of GF% over the whole range of irradiation whereas vulcanizates of SBR have attained the smallest.

The GF% values attained by blends lie also between these two extremes and they decrease systematically with increasing the content of SBR in the blend when comparing these values at the same irradiation dose. Moreover, GF% values attained by different vulcanizates increase with increasing irradiation dose; this latter behavior is of course, affiliated with increased extent of network structure. Apparently, this latter process, i.e., network formation takes place with an increased rate in case of NR vulcanizates with respect to SBR and mainly in the lower range of irradiation, namely between 50 kGy and 100 kGy. Moreover, the change in GF% values is a limited one as it increases from about 65% at 50 kGy to ~80% at 250 kGy for vulcanized NR rubber.

These data given above indicate clearly that the extent of the insoluble part in any vulcanizate increases with increasing irradiation dose as well as NR content.
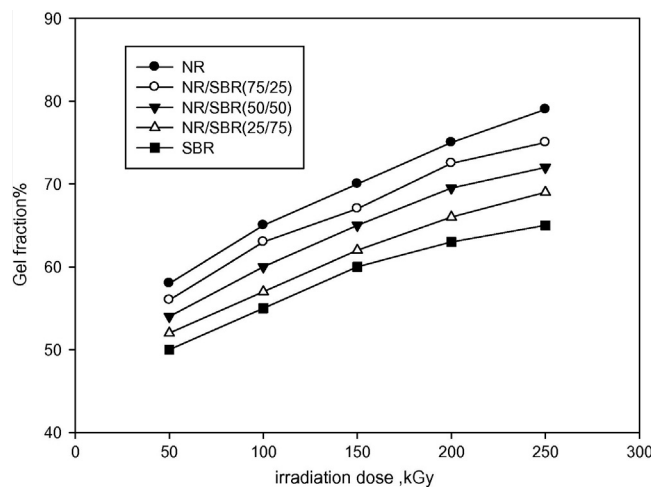

Figure 3 Effect of irradiation dose on the elongation at break % of NR, SBR and NR/SBR blends.

Figure 4 Effect of irradiation dose on the gel fraction% of NR, SBR and NR/SBR blends.

3.2.3. Swelling number SN

The results obtained for the variation of SN, for the two gum rubbers as well as their blends in benzene as solvent, as a function of the irradiation dose are shown in Fig. 5. It may be seen that SBR has attained the largest values of SN over the whole range of irradiation whereas NR has attained the smallest values. The blends have attained values that lie between these two extremes.
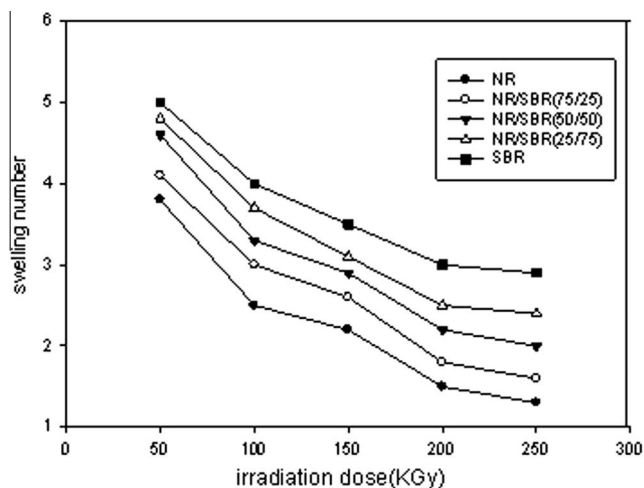

Figure 5 Effect of irradiation dose on the swelling number of NR, SBR and NR/SBR blends.
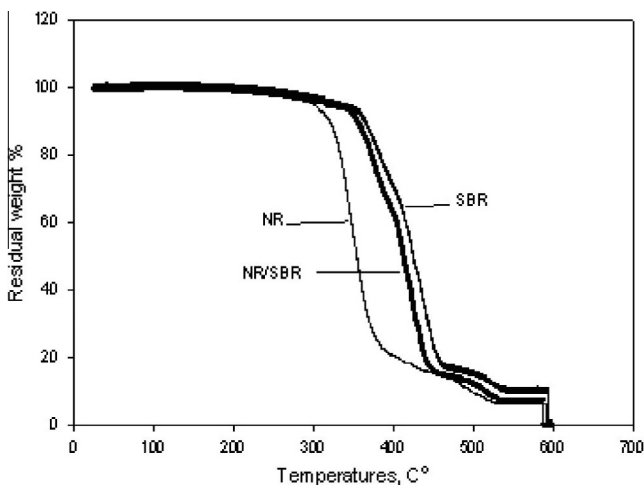

Figure 6 TGA thermograms of NR, SBR and NR/SBR (50/50) blend irradiated at 150 kGy.

Moreover, it may be observed that the value of SN of different rubber compositions decreases with increasing the radiation dose and with increasing the NR content in the blend. The first observation may be correlated with increased extent of crosslinking due to increased irradiation dose. On the other hand, the second observation is the attainment of NR vulcanizates of lower SN with respect to the ones attained by SBR and may be correlated with the increased rate of crosslinking of NR with respect to SBR.

3.3. Thermal stability properties

Fig. 6 illustrates the TGA thermograms of NR, SBR and the vulcanized NR/SBR (50/50) blend irradiated at 150 kGy, which show the variation of the residual weight% (RWP) of both gum rubbers as well as its blend with the temperature. It can be seen that all thermogravimetric curves exhibit at first a slight and gradual decrease in its RWP of ~4% over a temperature range of ~300 °C, which may be attributed to evaporation of volatile materials. This is generally followed by abrupt decrease in the RWP values of all compositions over a limited range of temperature, which accounts for a single degradation step that lie within the temperature range of 320–470 °C for the start and the end of the decomposition, respectively.

The thermal degradation temperature of pure NR is around 385 °C. The thermal degradation temperature of the blends increased with increase in addition of SBR. This may be probably due to the higher thermal stability of SBR compared to pure NR (Varkey et al., 2000; Wang et al., 2009). Crosslinking Density is an important factor affecting the thermal stability of vulcanized rubber. Higher crosslink density leads to better thermal stability because of the higher values of activation energy needed for thermal decomposition of vulcanizates. Thus radiation vulcanization improves thermal stability of the blends because of the presence of crosslinking.

The above mentioned observations are confirmed by the data given in Table 1 which shows the corresponding temperatures for 20%, 40%, 60%, 80%, and 100% weight losses of NR, NR/SBR (50/50) and SBR, respectively, as blending of SBR with NR resulted in improvement of the latter rubber in the blend.

4. Conclusions

From the results obtained in the present investigation, the following conclusions may be deduced:

- The tensile strength increased with an increase of NR content in the blend.

Table 1 The temperatures for different percentage of weight losses of NR, SBR and NR/SBR (50/50) blend vulcanized by irradiation dose at 150 kGy.

Sample	Temperatures at weight loss 20%	Temperatures at weight loss 40%	Temperatures at weight loss 60%	Temperatures at weight loss 80%	Temperatures at weight loss 100%
NR	328	343.5	355.4	385	400
NR/SBR (50/50)	367	402	417.6	435	465
SBR	382	414.6	432.4	462	479

- The improvement attained in mechanical properties has been certified by measurements of physical properties of the prepared blends.
- The magnitude of improvement is a function of the irradiation dose as well as the amount of natural rubber in the blend.
- The thermal stability of vulcanized NR/SBR blend (50/50) was improved.

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