

Influence of Electron Beam Radiation on Mechanical and Thermal Properties of Styrene-Butadiene-Styrene Block Copolymer

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Received 12 May 2008; accepted 8 August 2009

DOI 10.1002/app.31246

Published online 15 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Electron beam crosslinking of elastomers is a special type of crosslinking technique that has gained importance over conventional chemical crosslinking method, because the former process is fast, pollution free, and simple. The technique involves the impingement of high-energy electrons generated from electron accelerators and the subsequent production of free radicals on target elastomers. These radicals result in crosslinking of elastomers via radical–radical coupling. In the process, some chain scission may also take place. In this work, a high-vinyl (~ 50%) styrene-butadiene-styrene (S-B-S) block copolymer was used as the base polymer. An attempt was made to see the effect of electron beam radiation on the mechanical and thermal properties of the block copolymer. Radiation doses were varied from 25 to 300 kGy. Mechanical properties like ten-

sile strength, elongation at break, modulus at different elongations, hardness, tear strength, crosslink density, and crosslink to chain scission of the irradiated samples were studied and compared with those of unirradiated ones. In this S-B-S block copolymer, a relatively low-radiation dose was found effective in improving the level of mechanical properties. Differential scanning calorimeter and dynamic mechanical analyzer were used to study the thermal characteristics of the irradiated polymer. Influence of a stabilizer at different concentrations on the properties of S-B-S at varied radiation doses were also focused on. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2573–2581, 2010

Key words: electron beam radiation; thermoplastic elastomer; high vinyl S-B-S; stabilizer; mechanical properties

INTRODUCTION

Electron beam crosslinking of elastomers is a rapidly expanding technology resulting from some of the more important advantages it has over conventional chemical crosslinking. The process is fast, pollution free, and simple.^{1,2} Applications of this technology can further be explored in crosslinking of functional elastomers, where the easiness of crosslinking and subsequent specialized applications can bring about a tremendous positive impact in terms of finished product performance. In general, electron beam radiation in the range of 20–100 kGy is effective in bringing desirable changes in polymers.³ Crosslinking can be carried out under a wide range of conditions, including variation in the elastomer structure, the number, and type of reactive functional groups present in the elastomers to be cured, radiation

dose, temperature of crosslinking, surrounding atmosphere, and the presence of other chemicals in the form of additives incorporated within the elastomer matrix.

Electron beam crosslinking of elastomers have been reported in some comprehensive articles and textbooks. These research works were devoted to various aspects of the processes like kinetics, electron beam producing equipments, types of elastomers such as natural rubber (NR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), polychloroprene rubber (CR), fluorocarbon rubber (FKM), ethylene propylene diene rubber (EPDM),⁴ etc. and their applications.

The principle of electron beam crosslinking is based upon the formation of free radicals on the elastomer by impinging with high-energy electrons from electron beam generators and knocking out of labile hydrogen atoms from the elastomer and splitting of double bonds and subsequent oriented formation of covalent bonds through the coupling of these free radicals. In effect, a three-dimensional network through C–C bond is established.^{5–7} There is also significant improvement over quality control of the products in many directions in case of electron beam crosslinking.⁸

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Contract grant sponsors: Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy (DAE), Mumbai, India.

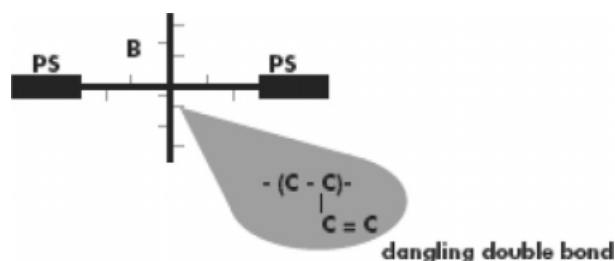


Figure 1 A two-dimensional structure of KRATONTMD-KX222 SBS block copolymer.

A thermoplastic elastomer (TPE) is a special type of polymeric material with properties and functional performance similar to those of conventional vulcanized rubbers at ambient temperature, yet can be processed in a molten condition as a thermoplastic polymer at elevated temperatures.⁹ A suitable crosslinking agent can crosslink a thermoplastic elastomer, which can well be electron beam radiation also.⁶ Structurally, such a crosslinked system is characterized by the presence of crosslinked rubbery phase and uncrosslinked plastic phase. The crosslinking improves the physical and chemical properties of the resulting thermoplastic vulcanisate (TPV). Electron beam (EB) of suitable radiation dose is a convenient means of crosslinking elastomers. However, literature survey indicates that application of EB crosslinking in case of high-vinyl S-B-S block copolymers is still not well explored. Although some research works in this field might have been done at industries, yet there is no evidence of openly published literature, which may be due to commercial sensitivity. When styrene-butadiene-styrene (S-B-S) block copolymer which is a TPE, is exposed to EB radiation, then along with crosslinking, some chain scission may also take place. Crosslinking to chain scission can be calculated and the ultimate properties may depend on these two opposing factors occurring simultaneously. Conventional S-B-S grades generally have about 8–10% of 1,2 (vinyl) groups in the mid block polybutadiene unit.

The main objective of this work is to study in details the influences of EB radiation at varied radiation doses on the mechanical and thermal properties of high-vinyl (~ 50%) S-B-S TPE. Stabilizers, for instance, antioxidants are commonly used to prevent the degradation of polymers due to the detrimental

effects of oxygen, and thereby, to effectively extend the useful lifetime of the polymer. The effect of an antioxidant on the mechanical properties of the polymer has also been studied.

EXPERIMENTAL

Materials

Styrene-butadiene-styrene (S-B-S) block copolymer Kraton DKX222 was obtained from Kraton Polymers, Belgium. It contains 18 wt % bound styrene and 82 wt % bound butadiene. The microstructure of the butadiene midblocks is about 50% 1,4 and 50% 1,2(vinyl) insertion in a random sequence. It has a density of 910 kg/m³ and weight average molecular weight (M_w) = 71,000.¹⁰ It is manufactured by polymerizing polystyrene-polybutadiene diblock, followed by coupling two (or more) living diblocks by di- (or multi-) functional coupling agent. Thus, it is a multiblock radial polymer. The structure of the polymer is shown in Figure 1.¹¹

Some of the more important features and benefits of Kraton DKX222 are as follows. It has high-vinyl butadiene midblock showing high reactivity to UV and EB radiation. The crosslinking reaction is fast and can be carried out in the absence of nitrogen blanket. The formulation principles are similar to those of conventional styrenic block copolymers. It is also seen from Figure 1 that there are dangling groups in the polymer main chains and these groups are due to 1,2(vinyl) insertion during polymerization.

Irganox B 215[®] used as the antioxidant was procured from Ciba Speciality Chemicals, Switzerland. It basically functions as a processing and a long-term thermal stabilizer and structurally is a synergistic blend of 67% Irgafos 168[®] and 33% Irganox 1010[®]. It has a density of 580 kg/m³.

Preparation of the batches

The compositions of the batches used for the study are given in Table I. The experimental variables were the radiation dose and the concentration of the antioxidant. A batch process, in a Haake Rheomix OS 600 (Germany), having a mixer chamber volume of 85 cm³, was used to mix all the batches. The batch

TABLE I
Batch Compositions, (in phr)^a

Components	$k_{0,0}$	$k_{12.5,0}$	$k_{25,0}$	$k_{37.5,0}$	$k_{50,0}$	$k_{100,0}$	$k_{200,0}$	$k_{300,0}$	$k_{12.5,1}$	$k_{25,1}$	$k_{37.5,1}$	$k_{50,1}$	$k_{100,1}$	$k_{200,1}$	$k_{300,1}$
S-B-S	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Antioxidant	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1
Radiation dose (kGy)	0	12.5	25	37.5	50	100	200	300	12.5	25	37.5	50	100	200	300

^a phr is parts per hundred rubber.

TABLE II
Mechanical Properties of the Compounds Irradiated with EB at Varying Dosages

Components	$k_{0,0}$	$k_{12.5,0}$	$k_{25,0}$	$k_{37.5,0}$	$k_{50,0}$	$k_{100,0}$	$k_{200,0}$	$k_{300,0}$
S-B-S	100	100	100	100	100	100	100	100
Dose (kGy)	0.0	12.5	25	37.5	50	100	200	300
Mechanical properties								
Hardness (Shore A)	23	34	40	42	44	49	57	60
Tensile strength (MPa)	5.3 (0.6)	6.4 (0.4)	8.6 (0.6)	6.7 (0.3)	6.4 (0.5)	3.9 (0.4)	3.0 (0.4)	2.4 (0.3)
Modulus 100% (MPa)	0.7 (0.05)	0.8 (0.05)	1.3 (0.06)	1.4 (0.08)	1.5 (0.04)	2.0 (0.06)	2.3 (0.08)	–
Modulus 200% (MPa)	0.9 (0.02)	1.2 (0.05)	2.1 (0.05)	2.2 (0.05)	2.6 (0.07)	3.4 (0.06)	–	–
Modulus 300% (MPa)	1.2 (0.05)	1.6 (0.04)	2.4 (0.06)	3.0 (0.03)	3.4 (0.05)	–	–	–
Elongation at break (%)	1120 (30)	1036 (60)	950 (28)	590 (32)	543 (18)	250 (26)	145 (16)	60 (12)
Tear strength (kN/m)	18.8 (0.3)	25.1 (0.3)	32.6 (0.5)	27.3 (0.6)	25.2 (0.4)	19.5 (0.8)	15.2 (0.6)	10.2 (0.7)
Crosslink density (mol/mL) $\times 10^5$	–	0.32 (0.02)	1.63 (0.08)	4.13 (0.04)	5.50 (0.07)	13.84 (0.08)	32.23 (0.03)	61.35 (0.06)
Tension set (%)	8.0 (0.2)	5.0 (0.1)	5.0 (0.2)	4 (0.1)	4 (0.1)	4 (0.1)	–	–

sizes were around 55 g. The mixer temperature was kept at 90–100°C. A constant rotor (cam type) speed of 65 rpm was applied. After 2 min of homogenization of the polymer masses, appropriate amount of the antioxidant was added and the mixing completed in 6 min. Immediately after each mixing, the composition was removed from the mixer, and while still in hot condition, passed once through a cold two-roll mill to achieve a sheet of about 2 mm thickness. The sheet was cut and pressed (2 mm) in a compression molding machine (George Moore press, UK), at 120°C, for 5 min and 3.94×10^4 kg/m² ram dia pressure. While molding, Teflon[®] sheets were placed between the sheet and the hot plates. The sheet was then cooled to room temperature by circulating cold water through the press plates.

Electron beam radiation

The sheets ($k_{12.5,0} - k_{300,0}$), ($k_{12.5,1} - k_{300,1}$), ($k_{25,3} - k_{300,3}$), and ($k_{25,5} - k_{300,5}$), having thicknesses of about 2 mm, were subjected to electron beam radiation of appropriate doses as shown in Table I. Electron beam radiation was carried out using an industrial ILU-6 accelerator from Budker Institute of Nuclear Physics, Russia, under the following conditions: energy = 1.6 MeV, average current = 2.5 mA, pulse frequency = 25 Hz, under aerated conditions at conveyor speed of 3 cm/s which delivered a dose of 12.5 kGy/pass as determined by nylon film dosimetry before radiation.

Preparation of test specimens

Test specimens were die cut from the cured sheets and used for testing after 24 h storage at room temperature. One sheet ($k_{0,0}$), as shown in Table I, was prepared as reference only through compression molding without exposing it to any radiation to compare the properties with those of radiation-cured ones.

Testing procedures

Tensile tests on the TPEs were performed according to ASTM D 412 on dumb-bell shaped specimens (Type 2) using a Hounsfield tensile testing machine H10KS (Germany) at a constant crosshead speed of 500 mm/min. Shore A hardnesses of the samples were measured using a Durometer type A, as per ASTM D 2240. Tear tests were performed according to ASTM D 624 on Type C specimens at a crosshead speed of 500 ± 50 mm/min and tension set tests were done according to ASTM D 412 with the same tensile testing machine. The average of three readings not varying within wide limits were taken and the results were reported on these average values, with corresponding values of standard deviations shown within parentheses at the side of the reported values. Crosslink densities were measured using the modified Flory Rehner equation by equilibrium solvent (here cyclohexane, which was chosen due to its solubility parameter of 8.18 (cal/cm³)^{1/2} which is close to that of butadiene units of S-B-S) swelling method, which is shown in eq. (1):

$$v = -\frac{1}{V_s} \times \frac{\ln(1 - V_r) + V_r + \chi(V_r)^2}{(V_r)^{1/3} - 0.5 \times V_r} \quad (\text{mol/mL}) \quad (1)$$

TABLE III
Percent Change in Properties with Variation of Radiation Dose

Radiation dose (kGy)	Tensile strength	100 % modulus	Elongation at break (%)
0.0	0	0	0
12.5	21	14	–8
25	62	86	–15
37.5	26	100	–47
50	21	114	–52
100	–26	186	–78
200	–43	229	–87
300	–55	–	–95

TABLE IV
Mechanical Properties of Unirradiated and Electron Beam Irradiated Polymers, Before and After Aging

Sample no.	Tensile strength (MPa)			Elongation at break (%)			Hardness (Shore A)		
	Before aging	After aging	% Change	Before aging	After aging	% Change	Before aging	After aging	% Change
$k_{0,0}$	5.3	4.1	-23	1120	998	-11	23	25	+8
$k_{25,0}$	8.6	5.4	-28	950	598	-37	40	41	+3
$k_{50,0}$	6.4	4.8	-25	543	402	-26	44	46	+5
$k_{100,0}$	3.9	2.3	-32	250	153	-39	49	52	+6
$k_{200,0}$	3.0	2.1	-30	145	98	-32	57	61	+7
$k_{300,0}$	2.4	1.2	-36	60	36	-40	60	61	+2

where, V_s = molar volume of the solvent used, χ = polymer-swelling agent interaction parameter (here, 0.3)¹² or Flory-Huggin's parameter, V_r is the volume fraction of the polymer in the swollen network, expressed as $V_r = 1/(A_r + 1)$ where A_r is the ratio of the volume of absorbed solvent to that of the polymer after swelling.^{13,14} Chain scission to crosslinking ratios were derived from Charlesby-Pinner equation^{15,16} which is shown in eq. (2):

$$s + \sqrt{s} = \frac{p_0}{q_0} + \frac{10}{q_0 \mu D} \quad (2)$$

where, s = sol fraction, μ = number average degree of polymerization, D = radiation dose in kGy, q_0 = density of crosslinking per unit dose in kGy, p_0 = density of main chain fractures per unit dose in kGy. In other words, p_0/q_0 = ratio of chain scission to crosslinking, $1/q_0$ is monomers per crosslink per kGy radiation dose, whereas, $1/p_0$ is monomers per chain scission per kGy radiation dose.

The glass transition temperature (T_g) was measured by a differential scanning calorimeter (DSC) Q 100 V8.1, TA Instruments (New Castle, DE), under nitrogen atmosphere at a heating rate of 10°C/min

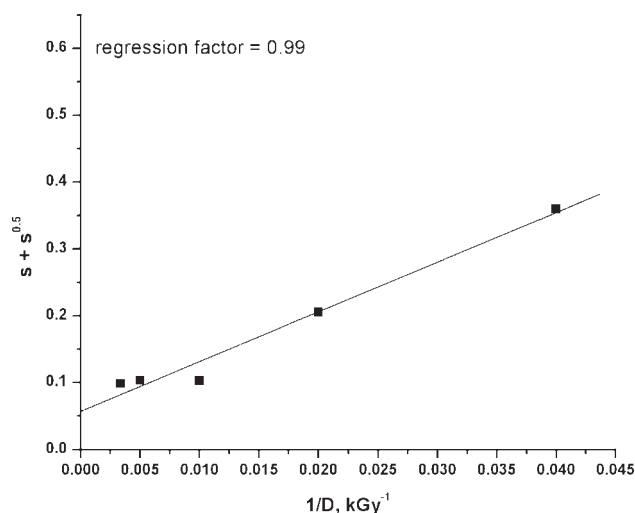


Figure 2 Charlesby-Pinner plot without antioxidant.

over a temperature range of -100°C to 150°C. The T_g was calculated from the inclination point of the first heating cycle. Dynamic mechanical properties of the samples were measured by a dynamic mechanical analyser (DMA) 2890, TA Instruments, under nitrogen atmosphere at a heating rate of 3°C/min over the same temperature range.

RESULTS AND DISCUSSION

Influence of EB radiation on S-B-S (in absence of an antioxidant)

Mechanical properties

The results obtained for the unirradiated and the irradiated samples are presented in Table II. It indicates that the ultimate tensile strength increases from 5.3 MPa for the unirradiated sample to a maximum of 8.6 MPa at 25 kGy and decreases with further increase in the radiation dose upto a minimum of 2.4 MPa at 300 kGy. The elongation at break shows a rapidly decreasing trend from an enormous value of 1120% for the unirradiated sample to a meager value of 60% at 300 kGy as can be seen from Table II. Modulus values at 100% elongation continuously increases from 0.7 MPa for the unirradiated sample to 2.3 MPa at 200 kGy as seen in Table II. Here, it is noteworthy to mention that at 300 kGy no value is observed, the elongation at break at this dose being only 60%. The hardness increases from 23 Shore A for the unirradiated sample to 34 Shore A at 12.5 kGy and reaches a maximum of 60 Shore A at 300 kGy. Tear strength also increases from the

TABLE V
 $s + s^{1/2}$ Values for Different Compounds as Function of Dose

Component ID	Radiation dose (D) (kGy)	1/D	$s + s^{1/2}$
$k_{25,0}$	25	0.04	0.36
$k_{50,0}$	50	0.02	0.21
$k_{100,0}$	100	0.01	0.10
$k_{200,0}$	200	0.005	0.10
$k_{300,0}$	300	0.003	0.09

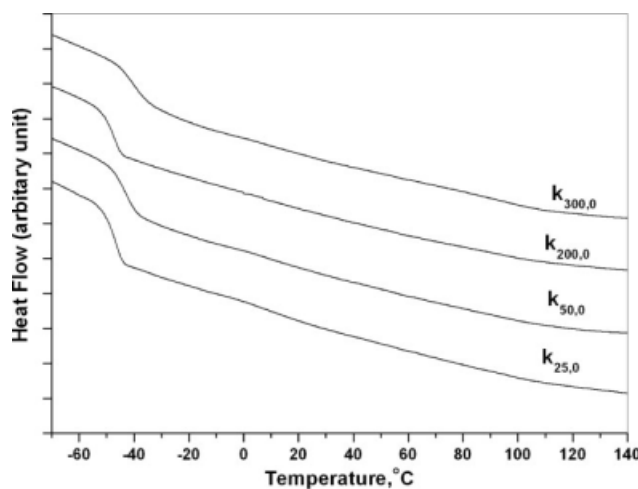


Figure 3 DSC thermogram of heat flow versus temperature for various compounds.

unirradiated sample to a maximum of 32.6 kN/m at 25 kGy and then decreases with further increase in radiation dose. There is not much change in the values of tension set though with increasing radiation dose there is a decreasing trend, indicating slightly better elastic recovery properties. It is also seen from Table II that the crosslink density as calculated from Flory Rehner equation continuously increases, almost linearly as a function of radiation dose from 0.3×10^{-5} mol/mL at 12.5 kGy to 61.3×10^{-5} mol/mL at 300 kGy. Table III shows the percentage change of physical properties such as ultimate tensile strength, modulus at 100% elongation, and elongation at break, the percentages calculated with respect to the unirradiated sample. Although the change in elongation at break is negative, which is rather desirable due to the initial unusually high value, yet the desirable positive changes for the other two parameters upto 50 kGy is observed. One important aspect is that at 25 kGy, the percent change in tensile strength is the maximum. After aging retention properties such as tensile strength and elongation at break without addition of an antioxidant are poor as observed from Table IV.

It may be mentioned here that generally mechanical properties are functions of crosslink density which in turn is function of radiation dose. The trends obtained for the mechanical properties are in

TABLE VI
Values of Glass Transition Temperature (T_g) from Differential Scanning Calorimetric (DSC) Studies

Sample no.	T_g of butadiene ($^{\circ}\text{C}$)
$k_{25,0}$	-48
$k_{50,0}$	-47
$k_{200,0}$	-43
$k_{300,0}$	-39

TABLE VII
Glass Transition Temperature (T_g) as Measured by Dynamic Mechanical Analysis (DMA)

Sample no.	T_g of butadiene ($^{\circ}\text{C}$)	Tan $\delta_{(\text{max})}$
$k_{0,0}$	-32	1.3
$k_{25,0}$	-31	1.7
$k_{50,0}$	-30	1.6
$k_{300,0}$	-23	0.8

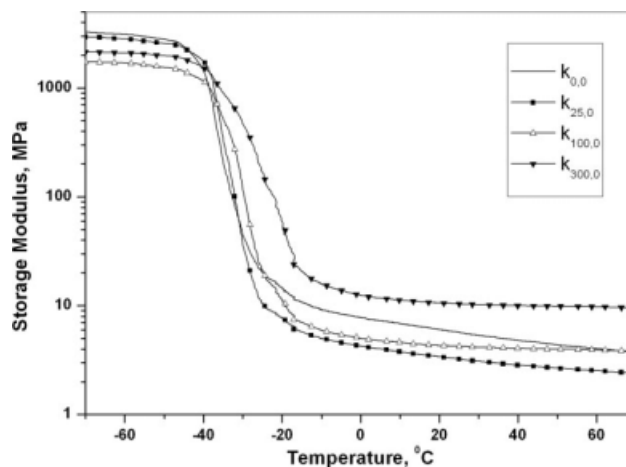


Figure 4 Storage modulus versus temperature for various compounds.

conformity with that usually encountered with many polymers and have been reported in many literatures and texts. These trends may be explained further by considering chain scission taking place simultaneously with crosslinking, when subjected to radiation.

A possible explanation lies in understanding of the change in the microstructure of the polymer molecules as a function of radiation dose. The increase in crosslink density calculated from Flory Rehner

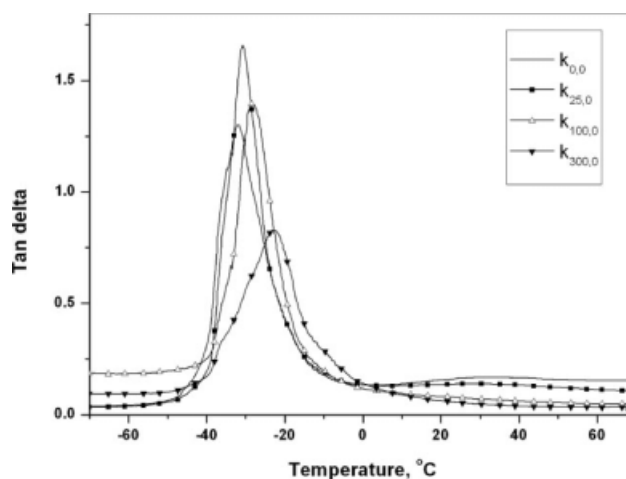


Figure 5 Tan δ versus temperature plot for various compounds.

TABLE VIII
Mechanical Properties of Electron Beam Irradiated Polymers, at 1 phr of the Antioxidant, Before and After Aging

Sample no.	Tensile strength (MPa)			Elongation at break (%)			Hardness (Shore A)		
	Before aging	After aging	% Change	Before aging	After aging	% Change	Before aging	After aging	% Change
$k_{25,1}$	7.6	6.2	-18	710	535	-24	42	42	0
$k_{50,1}$	5.6	4.8	-14	518	365	-30	45	45	0
$k_{100,1}$	3.4	2.7	-21	230	192	-17	51	51	0
$k_{200,1}$	2.8	2.3	-19	125	85	-32	57	57	0
$k_{300,1}$	2.1	1.7	-19	57	40	-30	60	62	+3

TABLE IX
Mechanical Properties of Electron Beam Irradiated Polymers, at 3 phr of the Antioxidant, Before and After Aging

Sample no.	Tensile strength (Mpa)			Elongation at break (%)			Hardness (Shore A)		
	Before aging	After aging	% Change	Before aging	After aging	% Change	Before aging	After aging	% Change
$k_{25,3}$	6.0	4.9	-18	640	508	-21	40	42	+5
$k_{50,3}$	4.3	4.1	-5	490	395	-19	45	46	+2
$k_{100,3}$	3.1	2.5	-19	200	145	-30	50	50	+0
$k_{200,3}$	2.6	2.1	-19	120	81	-33	56	56	+0
$k_{300,3}$	2.0	1.8	-10	50	35	-30	58	60	+3

equation with increasing radiation dose is further supported by Charlesby-Pinner plot, which is shown in Figure 2. Since the plot of $s + s^{1/2}$ against $1/D$ is linear, it can be inferred that with increase in D , the value of $s + s^{1/2}$ decreases. This means that with increasing radiation dose, the sol fraction decreases or conversely, the gel fraction increases, which is presented in Table V. An increase in gel fraction means an increase in crosslinking. From this plot, a positive value of p_0/q_0 (here 0.06) is obtained, indicating that along with crosslinking, chain scission also takes place. Since p_0/q_0 is the intercept of the straight line in the plot and is the ratio of chain scission to crosslink, it can be inferred that if the crosslink increases then chain scission also increases proportionately. It is then believed that at higher radiation dose, the main backbone of the polymer may break into many small fragments, i.e., many small clusters of crosslinks, each of the fragments housing higher number of crosslinks than that at

lower radiation dose. These small fragments can act as separate physical entities and the interfragmental forces are too small to hold them under externally applied large separating forces. The one body system with lower crosslink density as is realized under lower radiation dose is broken and yields under much lesser separating pressure. This, results in a rapid decrease in the magnitudes of tensile strength, elongation at break, and tear strength. An optimum is obtained, where the two opposing parameters via property enhancement through increasing crosslink density and weakening through increasing chain scission is balanced. An elaboration of the explanation of both, i.e., increase in modulus and decrease in tensile strength as a function of radiation dose, specifically at comparatively higher doses, i.e., between 25 and 300 kGy, is as follows. Tensile strength of a polymer is a function of crosslink density and energy dissipated, whereas modulus is a function of crosslink density only. Thus, with

TABLE X
Mechanical Properties of Electron Beam Irradiated Polymers, at 5 phr of the Antioxidant, Before and After Aging

Sample no.	Tensile strength (MPa)			Elongation at break (%)			Hardness (Shore A)		
	Before aging	After aging	% Change	Before aging	After aging	% Change	Before aging	After aging	% Change
$k_{25,5}$	5.5	4.4	-20	520	400	-23	41	44	+7
$k_{50,5}$	3.8	3.2	-17	370	315	-15	45	45	0
$k_{100,5}$	2.8	2.4	-16	160	123	-23	51	56	+10
$k_{200,5}$	2.3	1.8	-22	90	67	-26	58	61	+5
$k_{300,5}$	1.9	1.6	-18	45	40	-11	60	62	+3

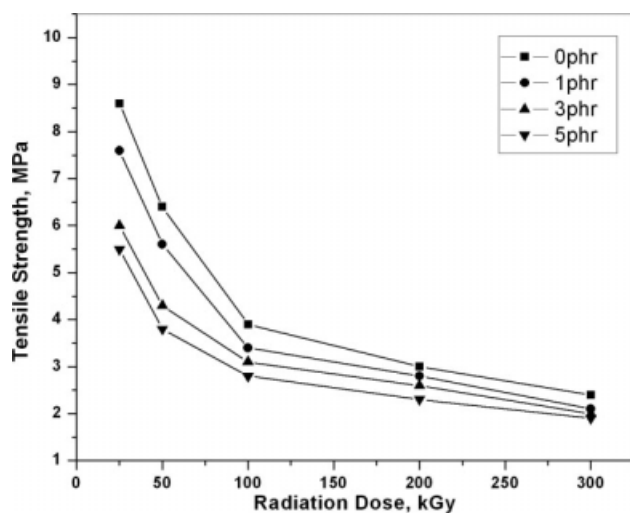


Figure 6 Effect of variation of radiation dose on tensile strength at various concentrations of the antioxidant.

increasing crosslink density, modulus continuously increases. On the other hand, tensile strength increases with crosslinks at lower crosslink densities only. This results in increase in tensile strength upto 25 kGy. However, at higher crosslink densities at higher radiation doses, the network becomes so dense that there is little scope of energy dissipation in the matrix and this energy supplied is rather used for breaking the bonds. At higher crosslink densities, the segments of the butadiene units become immobile, the system becomes stiffer and as a consequence the elasticity decreases. This results in drop in elongation at break also. In brief, a low value of p_0/q_0 which is nothing but the ratio of chain scission to crosslinking, reflects the enormous dominance of crosslinking over chain scission.

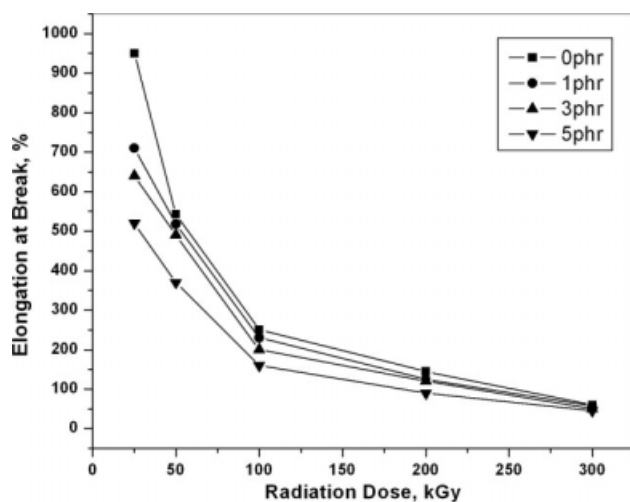


Figure 7 Effect of variation of radiation dose on elongation at break % at various concentrations of the antioxidant.

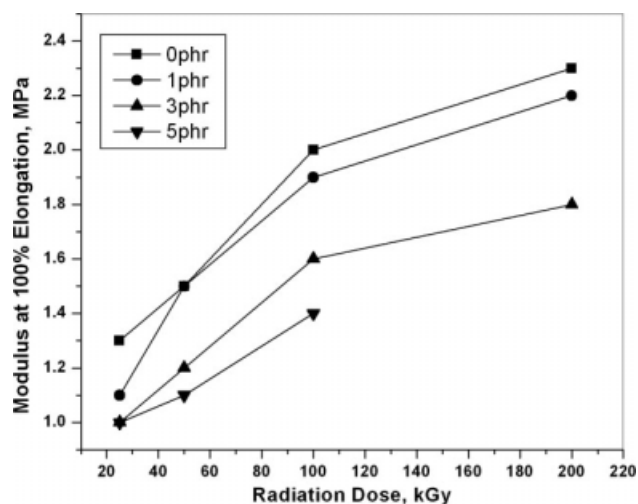


Figure 8 Effect of variation of radiation dose on modulus at 100% elongation at various concentrations of the antioxidant.

Thermal analysis

The DSC thermograms of the samples, irradiated at different radiations are shown in Figure 3. It is observed from the figure, that with increasing radiation dose, the T_g of the butadiene mid block is shifted to the high temperature as seen from Table VI, indicating the higher extent of crosslinking. The values of T_g obtained from the dynamic mechanical analyses of the irradiated samples as shown in Table VII, also support the DSC results. Figure 4 shows a plot of storage modulus as a function of temperature. It is found that with increase in radiation dose, the inflection point from the glassy Hookian to the rubbery plateau shifts to high-temperature side and the value of modulus also increases, indicating increased stiffness of the irradiated samples and higher extent of crosslinking. The $\tan \delta$ versus temperature plot,

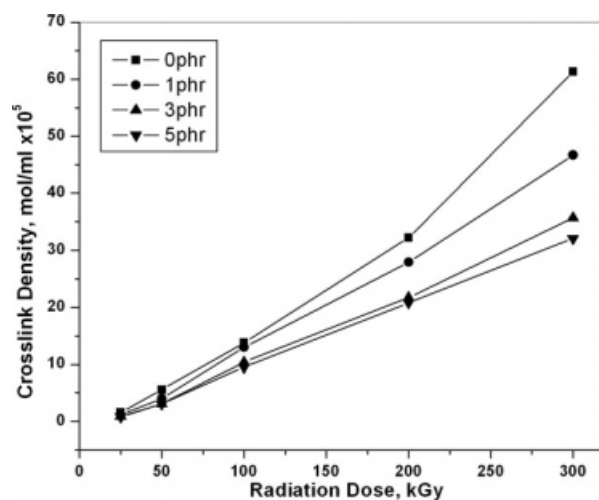


Figure 9 Effect of variation of radiation dose on crosslink density at various concentrations of the antioxidant.

TABLE XI
Percent Change in Properties with Variation of Radiation Dose at 1 phr of the Antioxidant

Radiation dose (kGy)	Tensile strength	100 % Modulus	Elongation at break (%)
0.0	0	0	0
12.5	15	0	32
25	43	57	-37
37.5	13	71	-51
50	6	114	-54
100	-36	171	-79
200	-47	214	-89
300	-60	-	-95

Figure 5 clearly shows a major transition at low temperature, (at around, -30°C) due to polybutadiene mid block. A second transition at high temperature (at around, $+110^{\circ}\text{C}$) is due to the polystyrene unit (not shown in figure). With increasing radiation dose from 25 to 300 kGy, the $\tan \delta_{(\text{max})}$ value for the butadiene unit gradually decreases and also shifts to the high-temperature side, clearly indicating the higher extent of crosslinking.

Influence of EB radiation in presence of an antioxidant

The results obtained with the incorporation of 1, 3, and 5 phr of the antioxidant are shown in Tables VIII–X, respectively. Here also the trends in the properties are the same as has been discussed earlier in the case without the antioxidant. It is seen from Figure 6 that the tensile strength continuously decreases with increasing radiation dose. The elongating at break values also decrease with increasing radiation dose as is depicted in Figure 7. Figure 8 shows the increasing trend in the values of modulus at 100% elongation with increasing radiation dose. The crosslink density, calculated by using Flory Rehner equation, rapidly increases with increasing radiation dose as is presented in Figure 9. Although the trends are the same, yet it is observed that with the incorporation of the antioxidant and increase in its concentration, the values of crosslink density at equivalent radiation dose as calculated from Flory Rehner equation is less. This is reflected in the lesser

TABLE XII
Variation of Radiation Dose and Corresponding $s + s^{1/2}$ Values at 1, 3, and 5 phr of the Antioxidant

Radiation dose (D) (kGy)	1/D (kGy ⁻¹)	$s + s^{1/2}$ at 1 phr	$s + s^{1/2}$ at 3 phr	$s + s^{1/2}$ at 5 phr
25	0.040	0.45	0.56	0.60
50	0.020	0.19	0.31	0.39
100	0.010	0.15	0.15	0.29
200	0.005	0.13	0.14	0.23
300	0.003	0.13	0.19	0.20

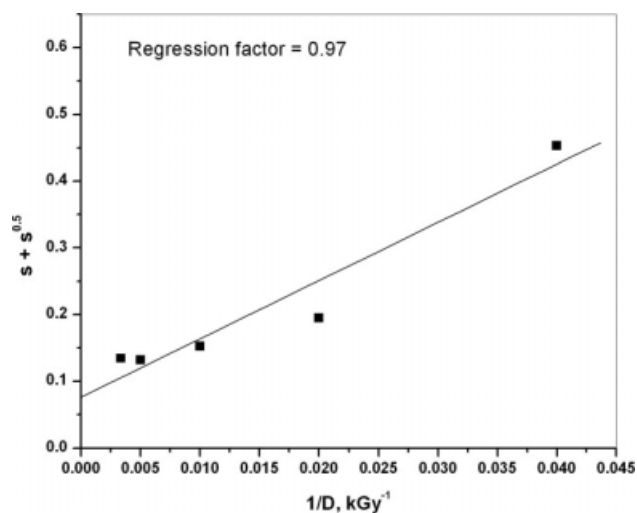


Figure 10 Charlesby-Pinner plot at 1 phr of antioxidant.

values of hardness and tensile strength. All other physical properties also show a decreasing trend with increasing amount of the antioxidant at equivalent radiation doses. On the other hand, the after aging retention properties as observed from Tables VIII–X representing 1, 3, and 5 phr of the antioxidant, respectively, are much improved with the incorporation of the antioxidant, though there is no significant improvement with the increase in its amount. Table XI is important in understanding the percent change in properties with variation in radiation dose at 1 phr of the antioxidant. It is interesting to mention that at 25 kGy, the percent change of tensile strength is the maximum, with a corresponding positive value of the percentage change in modulus at 100% elongation also. Above this radiation dose, though the moduli values show higher percentage changes, yet due to corresponding negative change in the tensile values, it is not advisable to mount to higher values of

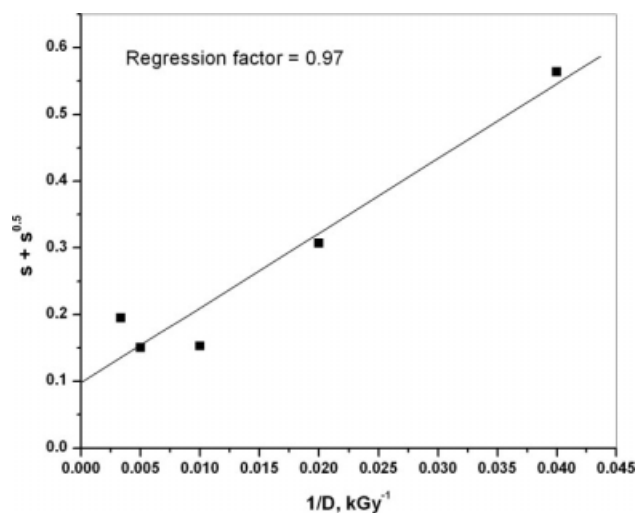


Figure 11 Charlesby-Pinner plot at 3 phr of antioxidant.

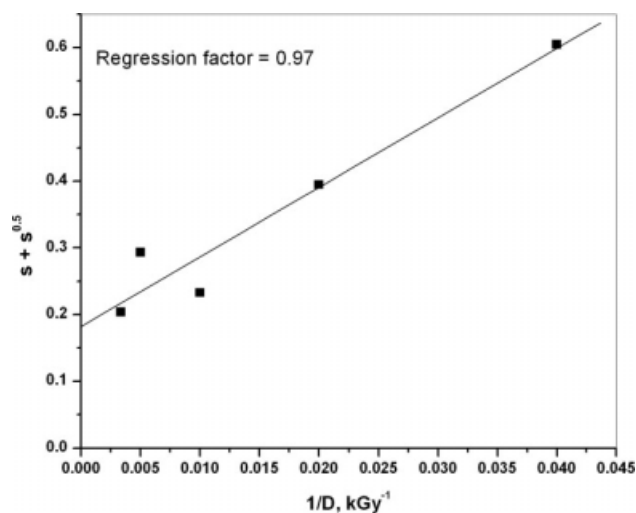


Figure 12 Charlesby-Pinner plot at 5 phr of antioxidant.

radiation dose. The same logic applies for the uncompounded samples abiding by Table III, which has already been discussed. Above 1 phr of the antioxidant, since the after aging retention properties show no significant improvements and thus it is quite advisable to restrict the amount of the antioxidant at this value. This is further supported when the Charlesby-Pinner plots at 1, 3, and 5 phr of the antioxidant are analyzed in details. The values of sol fractions at equivalent radiation doses for 1, 3, and 5 phr of the antioxidant increase as shown in Table XII. An increase in sol fraction means a decrease in gel fraction and decrease in crosslink density. The values of p_0/q_0 , at 0, 1, 3, and 5 phr of the antioxidant are 0.06, 0.08, 0.10, and 0.12, respectively, which are calculated from the Charlesby-Pinner plots (Figures 10–12). These are the ratios of chain scission to crosslinking and increase with increase in the concentration of the antioxidant. This suggests that with the incorporation of the antioxidant and increase in its concentration, extent of crosslinking decreases. The explanation may be that here the antioxidant influences radical-induced chemical reaction, resulting in lesser crosslinks. Again, during EB radiation, there is a possibility of the fragmentation of the main chains which are stabilized by absorbing active hydrogen from the antioxidant molecule and some other species. Hence, this results in stabilized-fragmented species, accounting for the increasing chain scission.

CONCLUSIONS

The influence of electron beam radiation doses from 25 to 300 kGy on the mechanical and thermal properties of a high-vinyl S-B-S block copolymer was studied in details. In this polymer system, a relatively low-radiation dose of 25–50 kGy was found optimum to achieve overall good mechanical properties. All the

results were a direct reflection of the two competing processes of crosslinking and chain scission, which is supported by the applications of Flory Rehner equation and Charlesby-Pinner plots. It is inferred that upto 25 kGy, the crosslinking dominated over chain scission, and thereafter upto 300 kGy, the reverse was true. However, further investigations like scanning electron microscopy and/or transmission electron microscopy are required to understand the change of morphology as function of absorbed dose. Furthermore, some rheological experiments like strain sweep and frequency sweep which are in progress might also support our results.

With the incorporation of the antioxidant, it was found that the crosslink density at equivalent radiation dose decreased. This phenomenon was explained through the influence of antioxidant on radical-induced chemical reaction, yielding lesser value of crosslinking. After quenching, the antioxidant became activated and donated hydrogen atoms to fragmented species of the main chain, in the process stabilizing the latter. Hence, an increase in chain scission was observed with the incorporation of the antioxidant.

The authors acknowledge Mr. Xavier Muyldermans, Kraton Polymers for his technical support.

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