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ORIGINAL PAPER

A study on dynamic rheological characterisation of electron beam crosslinked high vinyl styrene butadiene styrene block copolymer

Sanjoy Datta · Kinsuk Naskar · Y. K. Bhardwaj · Sunil Sabharwal

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Abstract Crosslinking of elastomers using electron beam radiation has several advantages over conventional method. It is accomplished much faster, in a more environmental friendly approach and in a much simpler manner. When fast moving electrons that are generated from electron accelerators are targeted on a polymer matrix, they primarily crosslink the polymer. However, in the process, some chain scission may also occur. In this work, a high vinyl ($\sim$50%) styrene–butadiene–styrene (S–B–S) block copolymer was used as the base polymer. Radiation doses were varied from 25 to 300 kGy. A detailed investigation was made to understand the effect of electron beam radiation on the rheological properties such as storage modulus, loss modulus, storage viscosity and complex viscosity of the block copolymer under strain and frequency sweeps performed in a Rubber Process Analyzer (RPA). Recyclability of the crosslinked S–B–S polymer was also explored by RPA and mechanical studies.

Keywords Thermoplastic elastomer · EB radiation · Viscoelastic behaviour · Recycling

Introduction

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 [1, 2]. A suitable crosslinking agent

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S. Datta · K. Naskar (✉)
Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302, India
e-mail: knaskar@rtc.iitkgp.ernet.in

Y. K. Bhardwaj · S. Sabharwal
BARC, Trombay, Mumbai 400 085, India

can crosslink a thermoplastic elastomer, which can well, be electron beam (EB) radiation also. Structurally, such a crosslinked system is characterised by the presence of crosslinked rubbery phase and uncrosslinked plastic phase. The influence of EB on the physical and chemical properties of various TPEs are reported by several authors [3–5] **i**ndicating improvements.

In this article, an investigation has been made on the effect of EB radiation on the rheological properties of a block thermoplastic elastomer of styrene–butadiene–styrene (S–B–S) type. The characteristic feature of the polymer lies in the fact that the mid-block polybutadiene unit consists of high vinyl insertion to the extent of about 50% as compared to conventional S–B–S, where the vinyl insertion is not more than 8–10%. These vinyl groups are more reactive than conventional double bonds towards EB crosslinking. Therefore, the material is of more interest in the field of research. When a polymer is irradiated with EB, then many kinds of reactions may occur within the polymer matrix [6]. The types of reactions depend on the complexity of the system and the dose of EB. Usually, two opposing reactions of crosslinking and chain scission compete with each other [7], and the final properties are determined through the dominance of one over the other. It has been already reported by the authors that EB radiation in the range of 25–50 kGy is an efficient means to produce an optimum level of crosslinking reflected through optimum mechanical properties for the material under study [8]. The characterisation of the products so obtained can be done mechanically, thermally, stereoscopically, morphologically, and in many other ways. The authors have already demonstrated in previous work through mechanical and thermal chacterisations, that the particular polymer under investigation is productive towards EB radiation [8]. In this work, rheological properties have been studied in detail using a Rubber Process Analyzer (RPA). RPA is a tool that can provide proper understanding of melt elasticity and processability of filled, crosslinked, compounded and also virgin polymers. These are understood in terms of the dynamic functions like dynamic moduli of elasticity and viscosity over a wide range of strain amplitude and frequency. When a sinusoidal strain is imposed on a linear viscoelastic solid, a sinusoidal stress response generally results. Under this condition, the dynamic mechanical properties depend only on temperature and frequency, and are independent of all types of deformations [9]. However, the situation is different in case of nonlinear viscoelastic solids, e.g., crosslinked thermoplastic elastomers. Then in addition, a dependence of the dynamic mechanical properties upon dynamic strain amplitude plays an important role [10]. This effect has prime importance for the engineering and design aspects of rubber components under dynamic loading like tyres, engine mounts, etc.

In this article, the dependence of dynamic functions such as storage modulus (G') and loss modulus (G'') on strain amplitude at a given frequency and also the dependence of complex modulus (G^*), storage viscosity (η') and complex viscosity (η^*) on frequency at a given strain amplitude have been studied. To understand the recyclability of the polymer, strain sweep was done first at a given elevated temperature followed by cooling the polymer and then heating to the same elevated temperature to carry out the second run. The results corroborated with the mechanical testing after recycling.

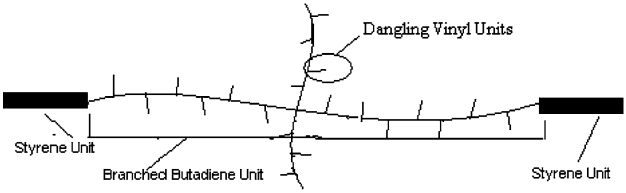

Fig. 1 A two-dimensional structure of high vinyl SBS block copolymer

Experimental

Materials

Styrene–butadiene–styrene (S–B–S) block copolymer Kraton DKX222 was obtained from Kraton Polymers, Belgium. It contains 18 weight percent bound styrene and 82 weight percent bound butadiene. The microstructure of the polybutadiene midblocks is about 50% 1,4(*trans*, *cis*) and 50% 1,2(vinyl) insertion in a random sequence. It has a density of 910 kg/m^3 and weight average molecular weight (M_w) = 71,000 g mol^{-1} [11]. The structure of the polymer is shown in Fig. 1 [12]. It is also seen from Fig. 1 that there are dangling groups in the polymer main chains and these groups are due to 1,2(vinyl) insertion during polymerisation.

Preparation of the batches

The experimental variable was the dose of radiation. A batch process, in a Haake Rheomix OS 600 (Germany), having a mixer chamber volume of 85 cm^3, was used to mix all the batches. The batch 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 6 min of homogenization of the polymer masses, the mixings were completed. 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 moulding machine (George Moore press, UK), at 120 °C, for 5 min and 4 ton/4″ ram diameter pressure. While moulding, 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 irradiation

The sheets ($k_{25,0}$, $k_{50,0}$, $k_{100,0}$, $k_{200,0}$ and $k_{300,0}$), having thickness of about 2 mm were subjected to EB radiation of appropriate doses. Here, k represents the polymer, followed by the numbers 25, 50, 100, 200 and 300 in subscript depicting radiation dose in kGy. The number 0 also in subscript means that no compounding ingredients were incorporated in the polymer under study. Elastomer samples of 2 mm thickness were irradiated in air with electron beam accelerator. Samples were placed in an adjustable speed conveyor belt and submitted to irradiation. Electron beam irradiation 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 0.03 cm/s, which delivered a dose of 12.5 kGy/pass as determined by nylon film dosimetry prior to irradiation. The number of crossings under the beam and their speed both define the irradiation dose, ranging from 25 to 300 kGy. The sample $k_{0,0}$ was kept as control, without subjecting it to any radiation.

Preparation of test specimens

Adequate amount of material was placed in the cavity of RPA 2000, which is basically a torsional dynamic rheometer. The cavity houses a biconical test chamber with grooved dies to avoid slippage of the material to be tested. It was closed through the action of a pneumatic ram operated at a pressure of 4 MPa and a slight excess of test material was needed to ensure that it was full. Tests were thus made under pressurised conditions, and therefore porosity did not develop in the samples when the instrument was under operating condition.

Testing programs

For the sweep studies, two test programs of the RPA were used. These programs are described in brief in the succeeding paragraphs.

Strain sweep

To study the extent and the nature of crosslinking of the radiation cured compounds, storage modulus (G') and loss modulus (G'') were measured as functions of strain. During the strain sweep, the temperature and the frequency were kept constant at 120 °C and 0.333 Hz, respectively. The range of the strain sweep was 0.56–1256%. In the strain sweep, after the first scan at 120 °C, the temperature was reduced to 50 °C, keeping the samples intact within the confines of the cavity of the RPA and again raised to 120 °C to carry out the second scan. This was done as a measure of recyclability test of the polymer.

Frequency sweep

Frequency sweeps were performed from 0.03 to 33 Hz to measure complex modulus (G^*), storage viscosity (η') and complex viscosity (η^*) as a function of frequency at 120 °C keeping the strain constant at 2.79%. The curves were studied to see the resemblances of the properties of the polymer with the inferences drawn from the curves obtained from the strain sweep.

Recylability test

After all the abovementioned were completed, the leftover parts of the EB cured samples were cut into small pieces and homogenised in a Haake Rheomix OS 600 (Germany) and moulded in the same manner as discussed in 2.2. Tensile testing were then performed without subjecting them further to any electron beam radiation (as was done in the previous case).

Tensile testing

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 cross-head speed of 500 mm/min. 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.

Results and discussion

The effect of amplitude dependence of the dynamic mechanical properties of uncrosslinked filled rubbers was first demonstrated by Payne (Payne effect) [10, 13]. He basically interpreted the sigmoidal decline from a "zero-amplitude" value of the storage modulus, G_0', to a high amplitude plateau G_∞' as a result of a breakage and reforming of physical bonds between filler aggregates (secondary structure) that was assumed to build an energetically elastic filler network within the soft rubber matrix. At large strains, this filler network breaks down and the modulus is then governed by polymer–polymer crosslinks (in rubber structure), elastically effective filler–polymer interactions and hydrodynamic filler effects. However, in this particular case of S–B–S block copolymer, the secondary structure is represented by the hard polystyrene units along with the entanglements in the coiled up mid-block polybutadiene units. The breaking down of the secondary structures at high strain amplitudes show similar analogy with the Payne effect, but the difference lies in the breaking of secondary structures at comparatively low strain amplitudes for the latter.

Strain sweep

The results obtained for the strain sweep are shown in Figs. 2 and 3. Analyses of these figures are elaborated as follows: Figure 2a is a plot of storage modulus (G') as a function of strain %, for variously radiation cured samples. The figure shows progressive non linear behaviour, i.e., a sigmoidal decrease with increasing strain amplitude, which is a typical characteristic of structure breakdown. When the temperature is raised to 120 °C, and the material in this condition is subjected to increasing strain, then two major changes can occur in the polymer. The first is the

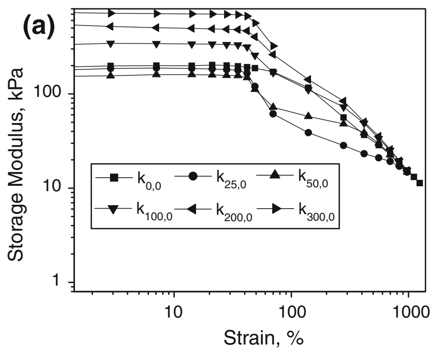

Fig. 2 Modulus as a function of strain (%). **a** Storage modulus; **b** loss modulus

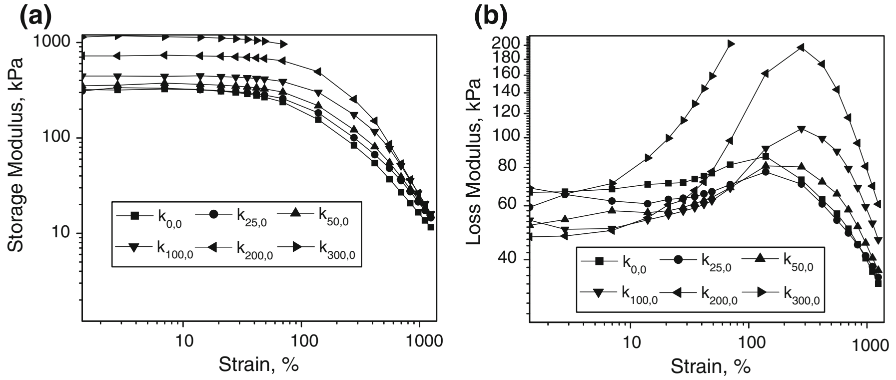

Fig. 3 Modulus as a function of strain (%) for recycled samples. **a** Storage modulus; **b** loss modulus

rapid uncoiling of the polybutadiene units and the other is the breaking down of the polystyrene units into smaller fragments. Thus, with increasing strain %, there is lesser resistance to both elastic deformation and viscous flow due to the mentioned changes. Thus, the sigmoidal decrease in the nature of the curves is explained. Finally at very high strain amplitudes, the breaking of the main chains and also the breaking of crosslinks that were established through exposure to radiation take place and the values of the storage moduli for all the samples converge almost at the same point. It is also clearly seen that at low strain amplitudes, the value of G' of the highest radiation cured sample (300 kGy) is significantly higher than those of lowly radiation cured ones (25 kGy and 50 kGy), or the one that has not been exposed to radiation, whereas the samples exposed to 100 and 200 kGy occupy intermediate positions between these two extremes. This trend is explained by the fact, that with increasing radiation dose, the crosslink density also steadily increases [8]. The drastic changeover point, marked by a sudden drop in values of the dynamic functions, of all the samples is almost at the same strain amplitude (50–70%) can be termed as “critical strain amplitude.” After the changeover, it is further observed that all the curves converge more or less at the same point, indicating that at very high strain amplitude, all the samples break down to the same extent. Figure 2b is a plot of loss modulus (G'') versus strain %. Here, the curves for all the variously radiation cured samples pass through a maxima. This can be explained by the fact that with increase in strain %, the resistance to flow first increases, attributed both to the presence of melt polystyrene domains and the presence of the coiled up mid block polybutadiene with chemical crosslinks obtained through EB radiation. Then after a certain point the material yields, i.e., breaks into smaller fragments, because of the breaking of the molten polystyrene into smaller fragments, slippage of the entangled polybutadiene chains and the breakdown of the chemical crosslinks. Here, it is important to mention that though polystyrene has a melting point much higher than 120 °C, yet in this polymer since the polystyrene blocks are of much lower molecular weight, they exhibit flow at this temperature. These small fragments, both in the molten and solid forms may offer less resistance to flow. The maxima of all the samples appear almost at the same value of strain %, but the value of the maximum for the sample exposed to 300 kGy is the highest with a decreasing trend seen with a decrease in radiation dose. This means that the highest radiation has also enhanced the highest degree of crosslinking. For the unirradiated sample, the value of the maximum is lowest because no crosslinking takes place there. From Table 2, it is seen that for the variously radiation cured samples up to a considerably high value of strain %, the values of storage modulus and complex modulus for a particular sample are nearly the same. With further increase in the strain % value the magnitude of the loss modulus increases at a faster rate than that of the storage modulus (not shown in the table). This means that initially the deformation is elastic and later it develops a more viscous nature. At high strain %, crosslink due to irradiation undergo drastic breakdown.

In the recycling experiments with the strain sweep, after the first scan at 120 °C, the temperature was reduced to 50 °C, kept at the reduced temperature for about 2 min, keeping the sample intact within the confines of the cavity of RPA 2000, and again raised to 120 °C to go for the second scan with each of the samples. The results of the second scan are shown in Fig. 3a and b. It is observed that even after such an operation on each of the samples, the nature of the curves for all the dynamic functions remain almost similar (as compared to Fig. 2), but with an increase in magnitude at corresponding strain percentages over the first run. The arguments for the materials scanned for the second time are the same as those of the first time scanned materials. The increase in the values of the storage modulus at corresponding strain percentages is due to a combination of various factors which needs some explanation. When the samples are cooled down to 50 °C, then they try to revert back to their original phase. While cooling down from the elevated temperature, the polybutadiene units try to coil up to their highest entropic state and simultaneously, the fragmented polystyrene units try to coalesce into bigger blocks. While these two phenomena take place, it may so happen that some of the polybutadiene units get trapped within the coalescing polystyrene domains. In effect, the cooled mass exhibits a changed molecular architecture of smaller polystyrene domains with some trapped polybutadiene units. When the temperature is again raised to 120 °C, there is more resistance to initial deformation because more number of polystyrene units form more physical

Table 1 Comparison of the values of $|G'|$, $|G^*|$ and η^* before and after the heat history for the samples irradiated at 25 kGy radiation

Strain (%)	Dynamic function, before			Dynamic function, after		
	$|G'|$ (kPa)	$|G^*|$ (kPa)	$|\eta^*|$ (Pa s)	$|G|$ (kPa)	$|G^*|$ (kPa)	$|\eta^*|$ (Pa s)
0.59 (low)	178.64	185.33	88579	307.93	313.77	150000
48.98 (intermediate)	119.96	132.92	63528	281.41	289.20	138000
139.89 (high)	38.76	58.70	28054	182.64	198.34	94794

associations. A little juxtaposition of the location of the curves for the dynamic function of storage modulus in the second cycle over the first one at relatively lower extents of radiation exposures (here 0, 25, 50 kGy) may be explained in the following manner. When the samples are cooled and again heated, the inbuilt stress histories of the samples are normalised and they all exhibit a more regular trend. What is more important is that a primary assessment of the possibility of recyclability of the uncrosslinked and the variously crosslinked samples has been done at this stage through these tests. A comparative study in dynamic functions between the first run and the second run is shown in Table 1. From the table, it is clearly understood that there is little enhancement in the all the properties after successive cooling and heating ageing indicating the possibility of good recycling. Though all the values are those in a molten state, yet due to increase in and closeness of the values of storage modulus (G') and complex modulus (G^*), a supposition at this point is that in the non molten state also, the polymer may show better tensile properties when subjected to real tensile testing according to ASTM D 412. Had the values of G' and G^* been not very close, then though after recycling G^* increases, yet governed by the equation $G^* = G' + iG''$, the loss modulus G'' would have contributed more to the magnitude of G^*. Then chain slippage would have been more and the expected trend would have been a lowering of the modulii values when subjected to tensile testing after recycling. The recyclability study of TPE has been reported by several authors [14]; however, literature is scanty in the area of recyclability of lightly EB crosslinked TPEs. Table 2 shows a comparative study of the moduli between the samples before and after recycling, done in a tensile testing machine. This real life comparison reflects the betterment of modulus for both the unirradiated as well as the samples irradiated at 25 kGy after recycling [8]. This was predicted from the melt rheology studies.

Frequency sweep

To understand the nature of the melt for the particular polymer in both uncrosslinked as well as lowly EB crosslinked forms, the samples were subjected to frequency sweep experiments. Figure 4 shows the dependence of complex modulus (G^*) on frequency. It is seen that the modulus increases with increasing frequency and also with increasing radiation dose. In general, the effect at high frequency is

Table 2 Mechanical properties of the compounds before and after recycling

Components	$k_{0,0}$, before	$k_{0,0}$, after	$k_{25,0}$, before	$k_{25,0}$, after	$k_{50,0}$, before	$k_{50,0}$, after
S–B–S	100	100	100	100	100	100
Dose, kGy	0	0	25	25	50	50
Mechanical properties						
Tensile strength (MPa)	5.3 (0.6)[a]	3.9 (0.4)	8.6 (0.6)	5.5 (0.6)	6.4 (0.5)	3.1 (0.4)
100% Modulus (MPa)	0.7 (0.05)	0.9 (0.03)	1.3 (0.06)	1.6 (0.05)	1.5 (0.04)	1.9 (0.07)
200% Modulus (MPa)	0.9 (0.02)	1.1 (0.03)	2.1 (0.05)	2.6 (0.03)	2.6 (0.07)	–
300% Modulus (MPa)	1.2 (0.05)	1.5 (0.04)	2.4 (0.06)	2.9 (0.07)	3.4 (0.05)	–
Elongation at break (%)	1120 (30)	610 (27)	950 (28)	398 (35)	543 (18)	176 (22)

[a] 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

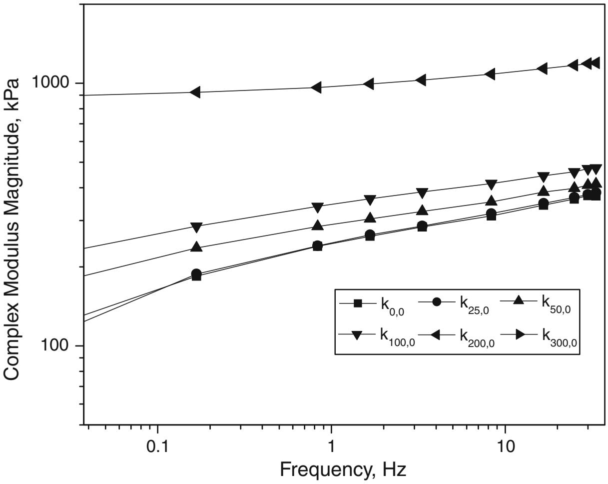

Fig. 4 Complex modulus as a function of frequency (Hz)

equivalent to the effect at low temperature generally obtained from dynamic mechanical analysis (DMA). Figure 5a shows the dependence of dynamic viscosity, η' on frequency for the unirradiated as well as for the samples subjected to various degrees of irradiation. The results show that η' decreases with increasing frequency. In the theory of viscoelasticity, the real component of the complex viscosity, $\eta^* = \eta' - i\eta''$, called the dynamic viscosity and characterizing the melt as a fluid, is related to the loss modulus G'', as $\eta' = G''/\omega$, whereas the imaginary component, η'', characterizing the melt elasticity, is related to the storage modulus G' by $\eta'' = G'/\omega$ [15, 16]. The dependence of complex viscosity as a function of frequency is depicted in Fig. 5b. Since all the samples show a decrease in viscosity with increase in frequency, which in turn is synonymous with shear rate, it is concluded that they are all non-Newtonian (pseudoplastic) in nature, when the melt rheology of the polymer is concerned. Finally, it is observed that for a given

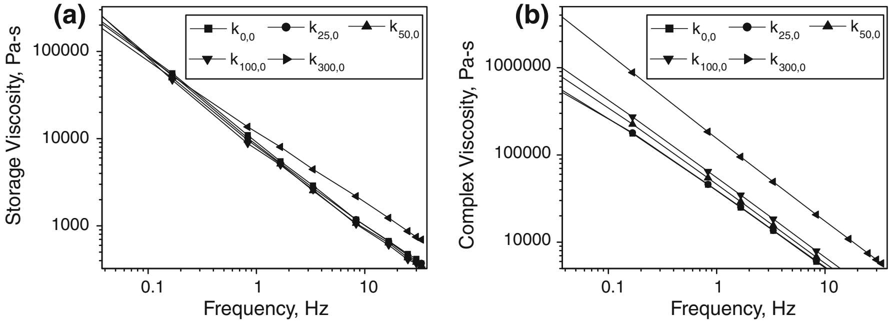

Fig. 5 Viscosity as a function of frequency (Hz). **a** Storage viscosity; **b** complex viscosity

frequency, the viscosity is the highest for the 300 kGy sample, again a reflection of the highest degree of crosslinking.

Conclusions

The influence of electron beam radiation doses from 25–300 kGy on the rheological properties of a high vinyl S–B–S block copolymer was studied in details. In this polymer system, the strain sweep showed higher initial values of storage modulus at higher radiation doses. Sigmoidal decreases of this parameter at a critical strain percent for all samples were observed. At very high strain percent, the values of the dynamic function were almost the same. This trend had an analogy with the so called Payne effect. The corresponding increase of the values of the dynamic functions in the second cycle was explained by the breaking up of the polystyrene domains and uncoiling of the polybutadiene chains at high shear rates during the operation and the reorientation of both during cooling. The molecular architecture before the second operation of the strain sweep was thus entrapped polybutadine coils within smaller domains of polystyrene. The physical interaction of the polystyrene domain was enhanced due to the generation of more surface area at smaller volumes of individual domains. The entrapped polybutadiene offered more resistance to initial deformation which was seen with higher values of dynamic functions in the second run of the strain sweep indicating good recyclability of the samples under experimental conditions. Finally, the tensile testing after recycling showed higher modulus values, thus establishing the possibility of recyclability. Increase in complex modulus was also observed as a function of frequency with the initial value being the highest for the sample exposed to the highest radiation dose. The complex viscosity exhibited a decreasing trend with increasing frequency, thus reflecting the pseudoplastic behaviour of both the unirradiated as well as the irradiated polymers.

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References

1. Legge NR, Holden G, Schroeders HE (1987) Thermoplastic elastomer: a comprehensive review. Hanser, Munich
2. De SK, Bhowmick AK (1990) Thermoplastic elastomers from rubber-plastic blends. Horwood, London
3. Marta P, Miroslawa EF, Puskas JE (2008) Radiation-induced degradation and crosslinking in elastomeric biomaterials. Elastomery 12(1):20–23
4. Danuta Z, Wanda M, Ryszard S (2003) Rheological properties of radiation-modified thermoplastic styrene elastomers. Polimery 48(9):620–626
5. Setiawan L, Schoenherr D, Mueller U (1995) Radiation-induced modification of the thermoplastic elastomers. Gummi, Fasern, Kunststoffe 48(10):700–707
6. Drobny JG (2003) Radiation technology for polymers. CRC Press LCC, Boca Raton
7. Bhowmick AK, Vijayabaskar V (2006) Electron beam curing of elastomers. Rubber Chem Technol 79:402
8. Datta S, Singha NK, Naskar K, Bhardwaj YK, Sabharwal S (2010) Influence of electron beam irradiation on mechanical and thermal properties of styrene-butadiene- styrene block copolymer. J Appl Polym Sci 115(5):2573–2581
9. Chatterjee K, Naskar K (2008) Study on characterisation and properties of nanosilica filled thermoplastic vulcanisates. Polym Eng Sci 48:1077–1084
10. Payne AR (1962) The dynamic properties of carbon black-loaded natural rubber vulcanisates. Part I. J Appl Polym Sci 6(19):53–57
11. Mayenez C, Muyldermans X. European Patent Specification, EP 0 696 761 B1
12. Brochure of Kraton: Kraton Fact Sheet, K0406
13. Lion A, Kardelky C, Haupt P (2003) On the frequency and amplitude dependence of the Payne effect: theory and experiments. Rubber Chem Technol 76:533–547
14. Nakason C, Worlee A, Salaeh S (2008) Effect of vulcanization systems on properties and recyclability of dynamically cured epoxidized natural rubber/polypropylene blends. Polym Test 27:858–869
15. Ferry JD (1980) Viscoelastic properties of polymers. Wiley, New York
16. Menard KP (2000) Dynamic mechanical analysis a practical introduction. CRC Press LCC, Boca Raton